REFINER
AND NATURAL GASOLINE MANUFACTURER

MARCH, 1936
Vol. 15, No. 3

A Gulf Publishing Company Publication
EDITED MONTHLY AT HOUSTON, TEXAS

Copyright, 1936

GEORGE REID
Editor

CONTENTS

An Economic Comparison of Coking and Cracking 85
W. L. Nelson

Interesting Operating Features in Stabilizer System 90
J. C. Albright

Continuous Acid Treatment of Cracked Distillate 94
J. S. Walton

Vacuum Equipment in the Oil Refinery, Part 2 98
Charles T. Chave

Experimental and Process Development Methods for Petroleum Oils, Part 2 104
L. C. Trescott

Combustion Phenomena in the Natural Gas Engine, Part 2 ... 110
Joseph Liston

Design of Routine and Semi-Routine Laboratories 114
Harry Vinock

Fractionation of Petroleum Residues and Heavy Crudes By Means of Natural Gas By Pilots Method 116
Dr. M. Naphtali

Nomographic Charts for Determining the Fliud Friction in Pipe Lines 120
H. V. Beck

Design of Vapor Recovery Plant and Treating Unit at Cushing . 123
J. C. Albright

Departments

The Look Box ..... 83 and 45a

Plant Activities 50a

Business Notes 54a

Ideas 59a

Science and Technology (Abstracts) 62a

New Equipment for the Modern Plant 75a

Catalogs and Bulletins 79a

Advertisers' Index 80a

SPECIALIZED OIL JOURNALS

Published by

GULF PUBLISHING COMPANY

OFFICE OF PUBLICATION
3301 Buffalo Drive, Houston, Texas

R. L. DUDLEY, *President*
A. L. BURNS, *Gen'l Manager*
S. W. ROBINSON, *Editorial Director*
J. KENT RIDLEY, *Managing Editor*

NEW YORK: Room 1023, 250 Park Avenue, Dick Swinsky, Manager.

PITTSBURGH: 902 Standard Life Building, W. W. Pigue, Manager.

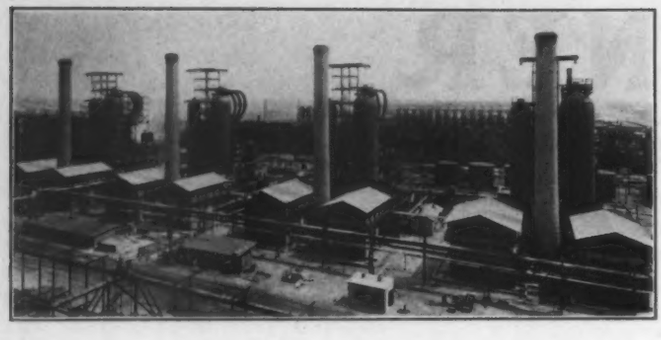
CHICAGO: Room 1834, 332 So. Michigan Ave., T. W. Nelson, Manager.

LOS ANGELES: 416 Haas Building, W. E. Green, Manager.

TULSA: 1020 Hunt Building, J. F. Carter, Jr., Manager.

FORT WORTH: 203 W. T. Waggoner Building, H. H. King, Manager.

Single copies 20 cents. Domestic subscription price $1.00 a year. Canada and Foreign subscription price $2.00 a year. Entered as second class matter June 16, 1923, at the post office at Houston, Texas, under act of March 3, 1879. Advertising rates on application.



Left: Four, large, two-stage refining units designed, constructed and installed by Foster Wheeler Corporation.

Complete Refinery Service

THE MOST EFFECTIVE EQUIPMENT for oil refinery use is designed and constructed for the specific requirements of each installation.

Foster Wheeler products, furnished individually or in groups, cover a wide range from single, small, heat exchangers to complete refineries in full operation.

Each individual piece of equipment is produced from the same laboratory, engineering, design, fabrication and construction facilities that would apply to a whole refinery unit.

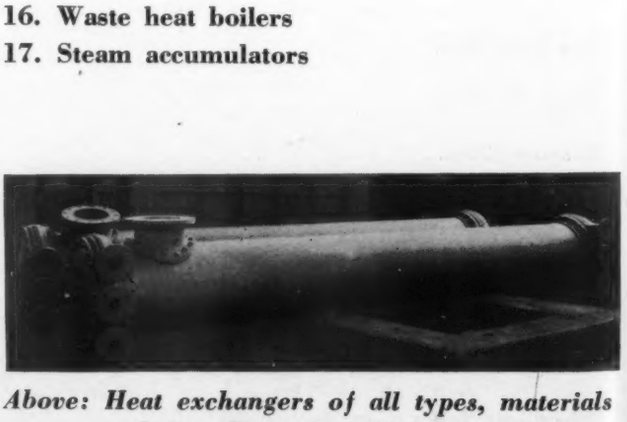
Unit responsibility for results and unified control of the engineering involved are essential for best results.

Among these highly developed products are:

1. **Tubular oil heaters**
2. **Fractionating towers**
3. **Heat exchangers**
4. **Coolers**
5. **Condensers**
6. **Steam jet vacuum pumps**
7. **Cracking heaters**
8. **Fusion welded shells**
9. **Absorption towers**
10. **Natural gasoline plants**
11. **Steam superheaters**
12. **Solvent extraction plants**
13. **Polymerization plants**
14. **Steam boiler plants**
15. **Economizers**
16. **Waste heat boilers**
17. **Steam accumulators**

Foster Wheeler Corporation

165 Broadway **New York, N. Y.**



Above: Heat exchangers of all types, materials and for all services.

VOLUME 15, No. 3 MARCH, 1936

REFINER
AND NATURAL GASOLINE MANUFACTURER
A GULF PUBLISHING COMPANY PUBLICATION

The Look Box

FOR the past several months the subject of Engineering Economics has been discussed from time to time in these columns. During this year THE REFINER, in furthering the theme of economics and engineering and technology as comrades steadily becoming more steadfast, has presented a group of important articles predominantly of the Engineering Economics type. And this work will continue to be presented in succeeding issues until, it is expected, practically all phases of refinery processes and equipments will be discussed from the technical, the engineering and the economic viewpoint.

"Chemomist"

Last month the thoughts of another editor relative to the kinship between technology and economics were reported here. Now comes Editor L. E. Westman of Canadian Chemistry and Metallurgy with another excellent thought, as expressed in his January issue, and he coins the name "Chemomist." "Slowly," he states, "the subjects of chemistry and economics are coming to be discussed at the same time in original studies. The procedure may be very complex, or it may be nothing more than the association of analytical results with current market prices.

"That ancient horror, really a type of unnecessary mental slavery, which so long prohibited the science-worker from an expression of the most elementary business, social or economic view, is passing. He soon will have attained the feeling that he has a normal right to an opinion. It may be some time before he will venture as far along this road, as many have gone, without anything but reasonably keen eyesight to guide them.

"There may be forces that attempt to withhold the science-worker from such exercises of the mind. Some tend to think of science as only an inanimate tool in the money world and the scientist as a sort of game-finder and retriever. Indications that the results of research studies might ever be extended into common economic observations by one and the same persons are considered as a kind of heresy; to be stamped out if possible. This may not be the common view, but it exists. The 'chemomist' then is with us; his struggle for definition, function and place has begun."

PETROLEUM products, which are taxed to provide more than half of the money required to build the nation's highways, also are used for highway construction, as is indicated by a survey of the United States Bureau of Public roads. The ratio, however, of value of petroleum products used and total taxes on products is so out of kilter that it is nothing to cite for the record. At any rate, it is estimated that for every $100,000,000 spent upon highways, $8,558,000 goes into petroleum products. That is about one-

Road Building

twelfth. The volume consumed amounts to 4,366,000 barrels. And of this total, 1,930,400 barrels, valued at $4,592,600, are used directly in highway construction. The others are consumed in the forms of fuels and lubricants by the various industries which supply road-building materials. That is rather a long way around to the point—but the petroleum industry does not nearly get its just share of the highway construction money. Activity in securing asphalt and road oil outlets for secondary road bed, better than nothing to be sure, is still not good selling.

A real campaign properly backed financially and with energy and enterprise to secure properly built road beds would increase consumption of road oils and other road materials to the point where current figures would soon look weak, if not actually sick. And there is little argument about the plausibility and the actual need for treating all road beds, all grades, everywhere, with road oils before the permanent road bed is laid—regardless of what type of permanent paving is used. Oil treated road beds and shoulders, properly treated, will increase the life and freedom from failure of permanent paving many times—and bring about a marked improvement in the market for road oils.

Books

DURING the past four or more years, members of the petroleum refining industry have been rather steadily requesting information regarding a good book on refinery engineering. Those with libraries of their own or with company or public libraries available are acquainted with the lack of modern information in book form. There has been a real need for some time for a modern book, or a series of modern books for use by those within the industry and for those planning on entering the industry or who are but recent entrants.

There is a feeling of real satisfaction to be able now to supply those requesting a modern book on petroleum refining—for W. L. Nelson's recently published "Petroleum Refinery Engineering" very definitely fills that need. A detailed review of this volume appears elsewhere in this issue.

There still is a distinct need for a book equally as well prepared as the one just mentioned dealing with natural gasoline manufacture—or requests from readers are not a good indication.

The past year or so has seen some other fine books offered those concerned with various phases of the industry. Those wishing late correlated data on motor fuels are referred to the two volumes by Nash and Howes, "Principles of Motor Fuel Preparation and Application" (1935). For those interested in the synthetic field, Carleton Ellis has prepared his excellent work, "The Chemistry of Petroleum Derivatives" (1934), and the same author added much to the literature with his two volumes, "The Chemistry of Synthetic Resins" (1935). For those "historically" inclined, and with a need for a volume tracing developments over a most interesting period, The Institution of Petroleum Technologists has published "Petroleum—Twenty-Five Years Retrospect" (1910-1935). Stagner and Kalichevsky, in 1933, prepared for the industry "Chemical Refining of Petroleum," the only book available dealing with this topic. For the technician interested in asphalt, Gaetz recently completed a valuable treatise on the specialized subject of "Water-White Hydrocarbons From Trinidad Asphalt" (1935).

This short report on modern books cannot include them all perhaps, nor does it include a number of valuable and recently revised handbooks of value to the engineer, nor such works as the Chemical Formulary. The discussion indicates, however, that no longer need those requiring knowledge of the industry in book form rely solely upon the publications of the period 1920 to 1924 or thereabouts. It is an indication of returning health to industry that new and modern works are being published and that workers in industry can again afford to gratify their need for such volumes.

Engineering Economics

THE scope of the group of important technical articles presented under the classification of Engineering Economics is ever widening. This issue brings presentation of more valuable contributions to that general theme—and some fine ones are scheduled for April publication.

In this issue W. L. Nelson presents another of his excellent analytical articles dealing with practices in coking and cracking, giving data offered as a guide as to when coking is profitable or unprofitable. J. S. Walton contributes a valuable discussion of the many phases of acid treatment of cracked distillates, which begins in this issue and is to be concluded in April. L. C. Trescott continues his discussion of experimental and development methods, this being the concluding installment. Charles T. Chave, whose important work on vacuum distillation has been so well received, concludes his discussion with data on vacuum jets and barometric condensers and offers suggestions in regard to solution of problems that frequently occur in refineries where vacuum distillation equipment is employed.

(*Please turn to page 45a*)

An Economic Comparison of

Coking and Cracking

W. L. NELSON, ***Consultant***
Professor of Petroleum Engineering,
University of Tulsa

THE high yield of gasoline secured when an oil is decomposed for coke formation encourages refiners to practice coking. However, the cost of operating a coking plant is high and only when gasoline prices are relatively high is it profitable to produce coke. From 1910 to 1915 coking was widely practiced but since that time gasoline prices have not been consistently favorable, and in spite of constant improvements in coke-producing processes, their use has not been standard practice.

The purpose of this article is to compare coking and cracking from an economic standpoint in order to isolate the factors that most greatly affect cost of coking-plant operation, to determine what market conditions are favorable for coking and to determine when coking becomes unprofitable. By means of Figures 2 and 3, and Equations 10 and 11, the refiner will be able to quickly judge whether coking or whether cracking is most profitable at current market conditions.

ENGINEERING ECONOMICS

IN VIEW of the constantly changing market prices of gasoline and fuel oil, it would appear that a combined coking and cracking plant would be the ideal equipment. Thus, if the gasoline price is high the plant could be operated for producing coke, but if the price of gasoline is low the plant can be operated as a cracking plant. The Dubbs process, when equipped with several coke chambers, is one of the few processes that is truly fitted for both coking and cracking. Another suitable process is the so-called Tubestill process[1]. To change the Tubestill process to a coking process only requires that the evaporator be replaced by several coke chambers or drums. The initial cost of either of the above process equipments is high because of the expensive coke drums but the additional plant cost can be repaid in a few weeks of profitable coking operation. The diagram shown in Figure 1 indicates a coking process that is similar in all essential features to the Tubestill process.

COKING PROCESSES

Although it is not the purpose of this paper to discuss the various coking processes, it is necessary to discuss them briefly so that there will be no doubt of the types of coking processing that are considered in the mathematical analysis that follows.

Coking was originally practiced in batteries of horizontal or vertical shell stills called coking-still-batteries. Usually each coking still was operated independently except that a common fractionating system was used for all of the stills. A charge of oil was slowly heated to about 800° F. and oil was admitted continuously at this temperature until a sufficiently thick coke deposit was produced. The feed then was discontinued and the still was heated to about 875° F., meanwhile using steam, for the purpose of drying the coke. The still was then allowed to cool and finally it was opened to remove the coke. The cycle was long, the thermal efficiency poor, the labor cost excessive, and the still-bottoms were a source of great expense and loss of time because the high temperature soon rendered them unfit for service. Various mechanical devices were utilized to remove the coke, such as steel frames which could be removed by cranes, revolving scraping devices, etc., but these were found to be only partially successful.

The process that is probably most widely used today is what may be called the Clean Recirculation process, as shown in Figure 1. In this process the heating of the coke chamber is accomplished by means of a continuously cycling stream of distilled gas oil and recycle stock. This feature eliminates the difficulties encountered in the coke still battery processes because of the externally fired vessels. In such vessels the coke deposit greatly impedes the transfer of heat, and as soon as a few inches of coke is produced the metal shell becomes red hot and the heating must be continued very slowly. In the clean recirculation process, all of the heat is delivered through pipe still tubes to a clean distilled stock and if the furnace is carefully designed, little or no coke is deposited in the tubes of the still. The Dubbs non-residuum operation and the remodeled Cross units which are operated for coke, employ essentially the same principles. The Clean Recirculation and the Dubbs non-residuum processes are the ones considered in the following economic analysis, although the general

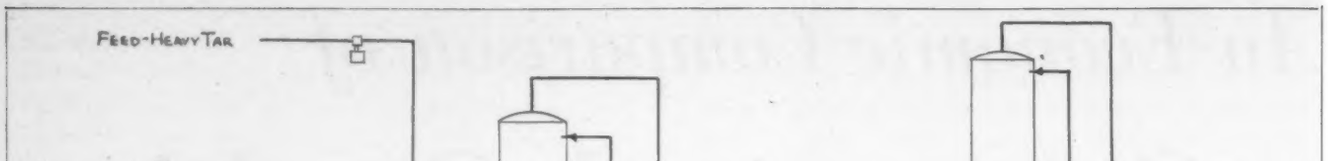


FIGURE 1
Modern Clean Recirculation Type of Coking Process. (From "Petroleum Refinery Engineering," by W. L. Nelson).

equations such as (7), (8), and (9) are applicable to any coking process.

In addition to the above common coking processes the Knowles Process[2] and the Knudsen Process[3] are attracting attention. In the Knowles Process special refractory-lined ovens which may be heated to 1200° F. are employed. Furthermore, the ends or doors of the oven may be quickly removed so that the red hot coke can be pushed from the oven by rams without waiting a long time for the oven to cool. The discussion that follows does not contemplate these new processes although the general equations may be used to study the processes if sufficient operating data are available.

YIELDS BY COKING AND CRACKING

In order to formulate a mathematical relation between market prices and operating characteristics, the yields of products that are produced by coking or by cracking must be obtained in a mathematical form.

Data for the yield of coke, as obtained from the current literature and private operating data, may be represented by the following equation:

$$\text{Yield of coke, tons per 1000 bbls.} = 61.85 - 1.17A_a \quad \text{(For black stocks)} \tag{1}$$

$$\text{Yield of coke, tons per 1000 bbls.} = 58 - 1.17A_a \quad \text{(For distilled stocks)} \tag{2}$$

in which: A_a = A.P.I. gravity of charge-stock

The yield equations for gasoline and tar[4] are as follows:

Cracking—

$$\text{Percentage of 400 E. P. gasoline by cracking} = 25 + 1.5\,(A_a - A_t) \tag{3}$$

$$\text{Percentage of fuel oil by cracking} = 75 - 1.95\,(A_a - A_t) \tag{4}$$

in which: A_t = A.P.I. gravity of cracked fuel oil.

Coking—

$$\text{Percentage of 400 E.P. gasoline by coking fuel oil} = 331 - \frac{42{,}450}{A_a + 131.5} \tag{5}$$

$$\text{Percentage of 400 E.P. gasoline by coking gas oil} = 303 - \frac{35{,}400}{A_a + 131.5} \tag{6}$$

ECONOMIC FACTORS

The only important factor that favors coking is the greater recovery of gasoline. Even this is not an advantage if the price of gasoline is low and the price of fuel oil is high. The future will doubtless bring a continued increase in the demand for gasoline and for distilled Diesel fuel oil, and hence we may expect that the value of residual fuel oil will never become an important factor. At any rate, if all of the coikng operations in the country were stopped, such a surplus of fuel oil would result that its price would drop sharply. Suffice here to say that if the price of gasoline is high with respect to the price of fuel oil coking tends to become profitable and vice versa. The value of the coke that is produced is very little compared to the value of these other products.

Operating factors that influence the profitableness of a coking or cracking process are: the cost of removing coke, the regular operating costs, the thermal efficiency of the processes, the cycle-time-efficiency that can be maintained, and the recycle ratio that must be used. The cost of removing and storing coke ranges from about $1 to $1.60 a ton and in many instances it is nearly equal to the value of the coke. Obviously if coke is produced in large quantities, the cost of removal and handling can be decreased greatly. By regular operating costs are inferred such costs as daily operating labor, supervision, replacements, repairs, steam, power, and depreciation. These costs are about equal for coking and cracking plants.

The thermal efficiency of a cracking plant is usually greater than for a coking plant by two influences—(1) the cracking plant operation is completely continuous so that heat-exchange can be used to advantage, (2) the coking chambers are operated intermittently so that all of the heat in the chamber and coke is lost when the coke is removed. However, this factor is not usually great and it involves only the cost of a small amount of fuel oil and a slightly larger capital investment in the coke still equipment. Most modern coking plants operate at about the same cycle-time-efficiency, and with the same recycle ratio, as cracking plants and hence these factors are almost negligible.

In this discussion the cycle-time-efficiency is defined as the days on stream times 100 divided by the

total of the days on stream and the days required for reconditioning of the plant equipment. As an example, a coking plant may operate for 95 days and then require five days for repair and cleaning. This is a cycle-time-efficiency of 95 percent. However, note that one of the several coke chambers may have been down for removal of coke at about two-day intervals during the 95 days on stream. The cost of removing coke can be handled most easily as a separate cost which has no connection with the cycle-time-efficiency.

Although the lesser factors have been neglected in much of the discussion that follows, the precise effect of the factors can be determined by using the three fundamental equations (7), (8), and (9).

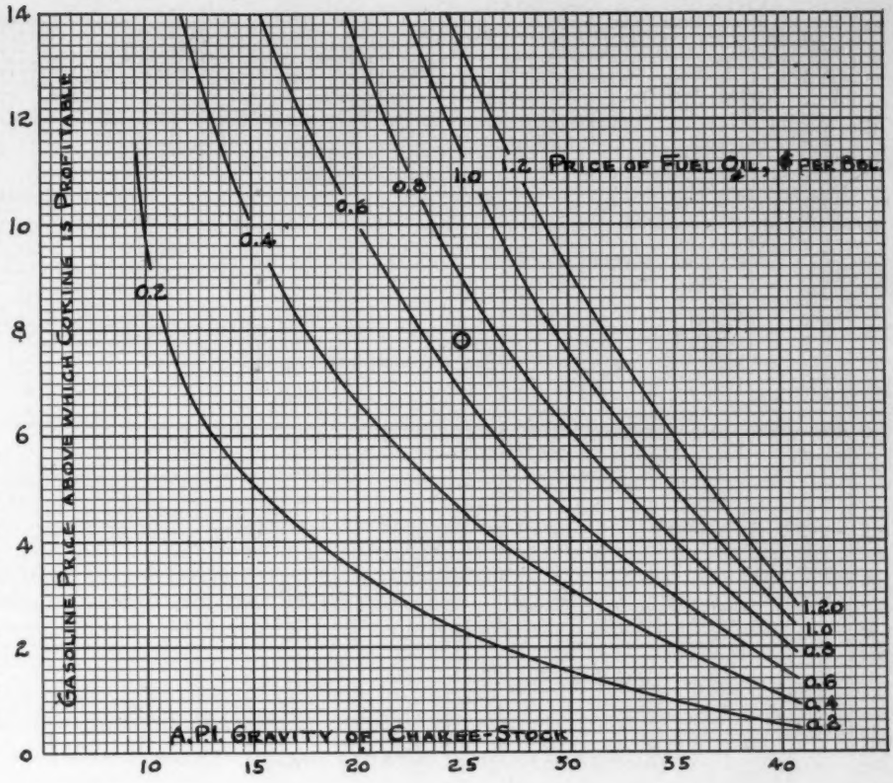


FIGURE 2
Gasoline price at which coking begins to be profitable.

PROFIT BY COKING AND CRACKING

The profit derived when a barrel of fuel oil is cracked, is:

$$\text{Profit} = \left\{\begin{array}{l}\text{value of gasoline}\\ \text{value of fuel oil}\\ \text{value of gas}\end{array}\right\} - \left\{\begin{array}{l}\text{regular operating costs}\\ \text{costs due to thermal efficiency and recycle ratio}\\ \text{costs due to shut-down time}\\ \text{cost of charge-stock}\end{array}\right\}$$

Basis: 1 barrel of charge-stock.

Item	Mathematical Expression	Meaning of Symbols
Profit by cracking=	P_F	($ per bbl. of charge stock)
Value of gasoline=	$\frac{42}{10000}\left[25+1.5(A_s-A_t)\right] V_g$	(V_g=gasoline price, cents per gal.)
Value of fuel oil=	$\frac{1}{100}\left[75-1.95(A_s-A_t)\right] V_f$	(V_f=fuel oil price,$ per bbl.)
Value of gas=(usually negligible in an economic study)		
Regular operating costs=	C_r	
Costs due to thermal efficiency and recycle ratio=	$\frac{D_F V_f R_F}{17500 \times 8.33 \times 42 SE_s}$	(D_F=Btu absorbed per bbl. of furnace charge-stock) (R_F=recycle ratio) (S=sp. gr. of fuel oil) (E_s=thermal efficiency ÷ 100)
Costs due to shut down time=	$(1-E_c)\,C_d$	(E_c=cycle-time-eff. ÷ 100) (C_d=shut-down cost per daily bbl.)

Using the above symbols:

$$P_F = [0.105 + 0.0063\,(A_s - A_t)]\,V_g + [0.75 - 0.0195\,(A_s - A_t)]\,V_f - C_r - \frac{D_F R_F V_f}{6{,}120{,}000 S E_s} - (1 - E_c)\,C_d - V_s \quad (7)$$

The profit when conducting coking processing can be formulated in much the same manner. However, the following additional factors and symbols are necessary.

$$\text{Cost of removing coke} = \frac{1}{1000}\,(61.85 - 1.17A_s)\,C_c$$

C_c = cost of removing coke, $ per ton
P_c = profit by coking, $ per barrel
D_c = B.t.u. absorbed per barrel of coke still charge-stock
R_c = recycle ratio for coking plant
V_c = value of coke, $ per ton.

The other symbols have the same meaning as for cracking processing but lower case letters are used to designate coking.

$$P_c = \left(1.39 - \frac{178}{A_s + 131.5}\right) V_g + (0.06185 - 0.00117A_s)\,(V_c - C_c) - c_r - \frac{D_c R_c V_f}{6{,}120{,}000 S e_s} - (1 - e_c)\,C_d - V_s \quad (8)$$

GASOLINE PRICE AT WHICH COKING BECOMES ECONOMICAL

The value of gasoline at which coking or cracking nets the same profit is the demarkation line at which coking begins to be profitable. This value of gasoline can be determined by setting Equations (7) and (8) equal to each other and solving for V_g—

However, in most cases many of the terms in this equation can be neglected. For example, the still efficiency and the recycle ratio are often nearly the same in cracking and coking plants, or the regular costs of operation will be the same.

$$V_g = \frac{(0.06185 - 0.00117A_s)\,(V_c - C_c) - [0.75 - 0.0195\,(A_s - A_t)]\,V_f - (c_r - C_r) - \frac{V_f}{6{,}120{,}000 S}\left(\frac{D_c R_c}{e_s} - \frac{D_F R_F}{E_s}\right) - (E_c - e_c) C_d}{0.0063\,(A_s - A_t) + \frac{178}{A_s + 131.5} - 1.285} \quad (9)$$

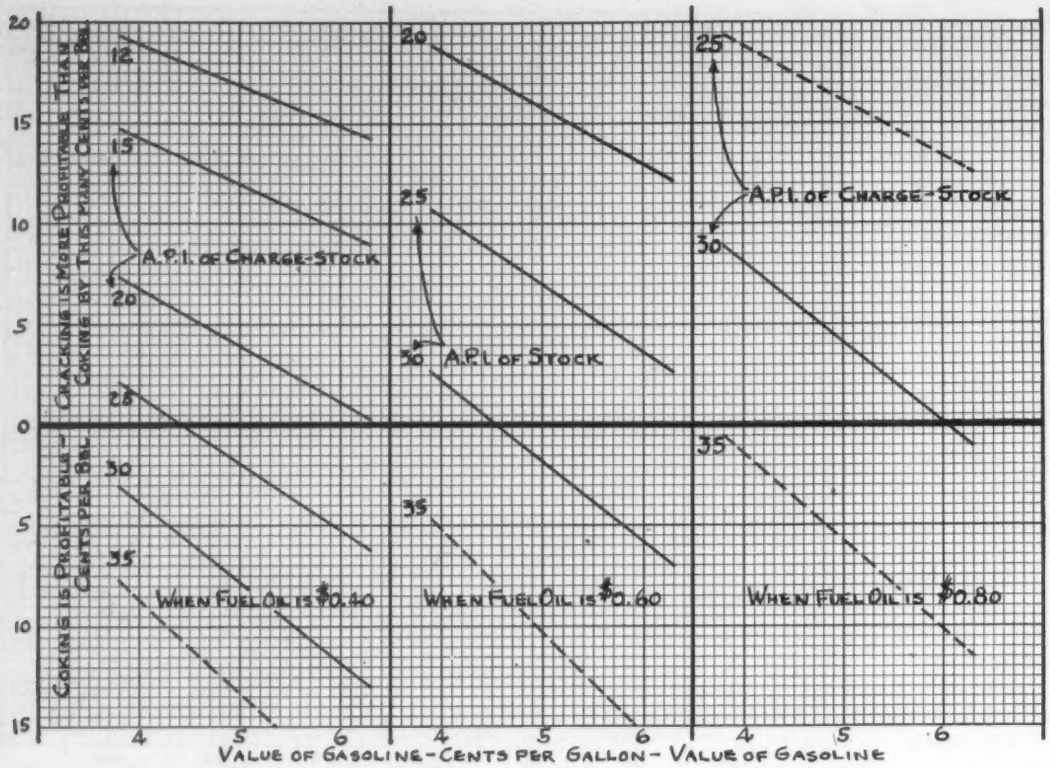

Cracking is More Profitable Than Coking by This Many Cents per Bbl.
Coking is Profitable Than Cracking by This Many Cents per Bbl.
A.P.I. of Charge-Stock
A.P.I. of Stock
When Fuel Oil is $0.40
When Fuel Oil is $0.60
When Fuel Oil is $0.80
Value of Gasoline-Cents per Gallon-Value of Gasoline

FIGURE 3
Loss incurred by operating a coking process when cracking is more profitable, and vice versa.

Thus, for many purposes the following simplified equation is adequate:

$$V_g = \frac{[0.0195(A_s - A_t) - 0.75]\,V_t}{0.0063\,(A_s - A_t) + \dfrac{178}{A_s + 131.5} - 1.285} \qquad (10)$$

This equation can be easily handled because it involves only the gravities of the charge-stock and the fuel oil, and the value of the fuel oil.

Equation (10) is plotted in Figure 2 as a function of the value of fuel oil and the gravity of the charge-stock.

LOSS INCURRED BY COKING WHEN COKING IS NOT PROFITABLE

The loss in dollars per barrel of charge-stock that is incurred by practicing coking when it is not profitable (or cracking when it is not profitable to crack) can be determined by subtracting equation (8) from equation (7), thus:

$$P_F - P_c = (A_s - A_t)\,(0.0063V_g - 0.0195V_t) + \frac{178V_g}{A_s + 131.5} - 1.285V_g + 0.75\,V_t \qquad (11)$$

Equation (11) is the simplified form in which many of the terms have been neglected. If the value of $P_F - P_c$ is positive, it is profitable to crack rather than to coke, and inversely, if $P_F - P_c$ is negative, coking is the more profitable operation. This equation is presented in graphical form in Figure 3.

USE OF FIGURES 2 AND 3

The value of cracked gasoline and of heavy fuel oil in Oklahoma during January, 1936, will serve as a basis for examining the charts. The market price of gasoline was 5.7 cents per gallon and of reduced crude oil or fuel oil, about 0.7 dollars per barrel.

Using a gravity of 25, and referring to Figure 2, the circle point indicates that the gasoline price must be 7.8 cents per gallon in order to make coking a profitable operation. The price of fuel oil would have to drop to about 50 cents per barrel to make coking a profitable operation when the gasoline price is 5.7 cents per gallon. Inasmuch as a large volume of fuel oil is actually being sold at or near 50 cents a barrel, it appears that coking is now on the border line between being profitable and unprofitable. By inspection of equation (9) it becomes apparent that a particular refiner might be able to practice coking at the present market conditions. As an example, a particular refiner may find that the item which involves the value of coke and the cost of removing it may make his coking plant profitable. Thus if the value of the coke is $1.50 a ton more than the cost of removing coke, this item will contribute about five cents per barrel of charge-stock in favor of coking and tend to make coking a profitable operation. The same applies to other factors which were neglected in equations (10) and (11) and Figures 2 and 3.

Figure 3 will aid in estimating the loss or profit that accrues by operating a cracking plant rather than a coking plant at the present market conditions. By referring to Figure 3 it appears that the profit by cracking when fuel oil is worth 60 cents, and when processing a 25 A.P.I. stock, is about 4.6 cents per barrel of charge-stock or 14.2 cents for 80-cent fuel oil. For 70-cent fuel oil, the average of these, or 9.4 cents per barrel of charge-stock is the profit that is gained by operating a cracking plant rather than a coking plant at the present market conditions. Note again that more accurate and detailed results can be obtained by the use of equations (7), (8) and (9).

GENERAL PROCESSING METHODS

Some refiners have adopted a method of running to coke which involves distilling the reduced crude oil to produce gas oil, cracking the gas oil into gasoline and fuel oil, and then coking the two residues, i.e., the straight-run tar and the fuel oil from the cracking plant. Perhaps the main reason for such an operation has been that cracking equipment performs much more satisfactorily on a distilled rather

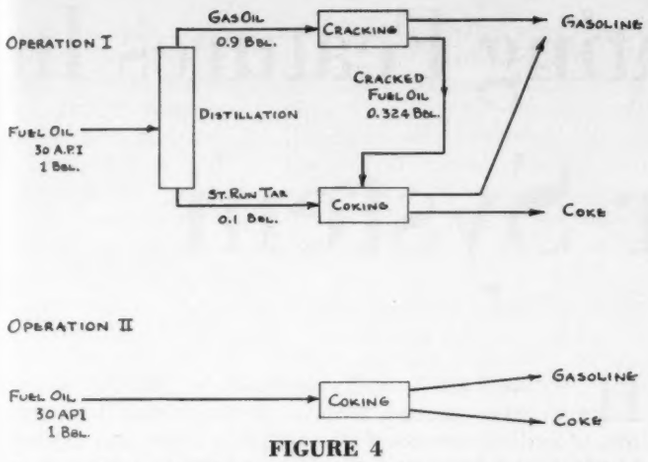


FIGURE 4

Two methods of reducing to coke. The comparison of these two processes is presented in the text.

than a black charging-stock. This made it necessary to dispose of the cracked and straight-run tar in some manner and the coking process was adopted for this purpose. In such an operation the final products are coke, gasoline, and gas.

Another manner of obtaining the same final result would be to coke the reduced crude oil directly, in a suitable recirculation type of process. Equations (7) and (8) afford a means of comparing the relative costs of the two above methods of reducing to coke. The operation of distilling, cracking, and then coking is referred to as Operation I, and running directly to coke is referred to as Operation II. These operations are shown in Figure 4.

If a 30 A.P.I. fuel oil is distilled to produce 90 percent of 32 A.P.I. gas oil and 10 percent of 12 A.P.I. straight-run fuel oil, and the 10 percent of fuel oil along with 32.4 percent of fuel oil obtained by cracking the gas oil, is reduced to coke, the following equation results:

$$P_{II} - P_I = 0.0184V_g + 0.00655(V_c - C_c) + 0.324\,C_r + 0.13\frac{D_F R_F V_f}{6{,}120{,}000 SE_s} + 0.324\,(1 - E_c)\,C_d - C_g \qquad (12)$$

in which: P_{II} = profit by Operation II
P_I = profit by Operation I
C_g = cost of producing gas oil by distillation

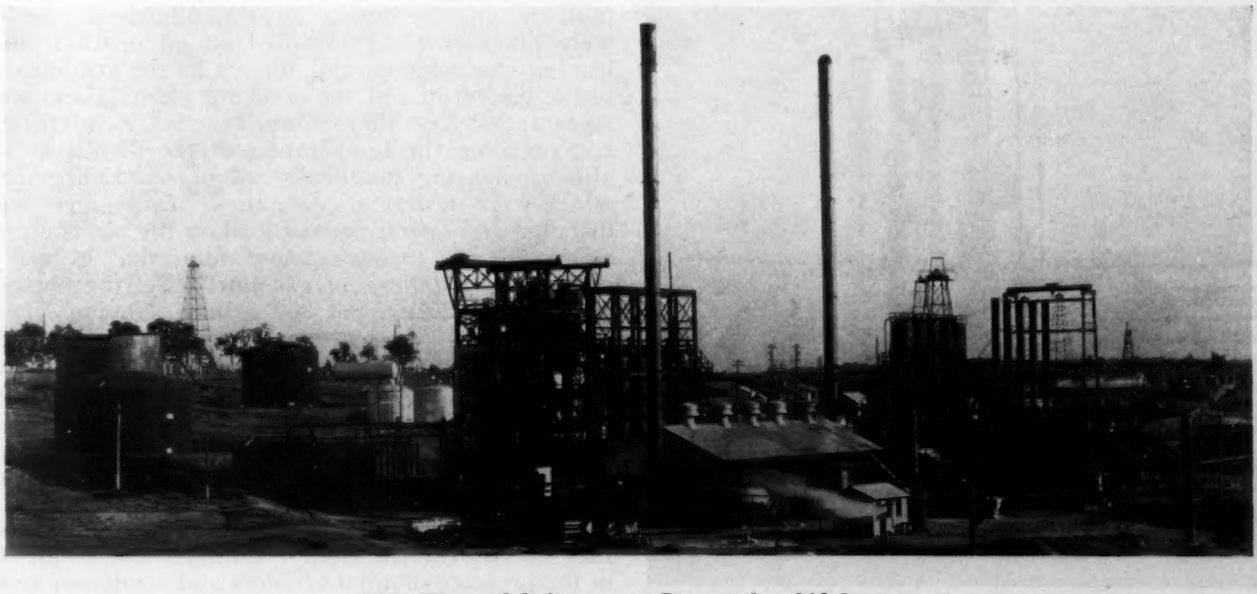
The operation of the cracking plant and the coking plants were assumed to be the same except that a recycle ratio of 3.1 was required in the coking plants whereas a recycle ratio of 2.5 was satisfactory in the cracking plant. Also, the efficiency of the coking still was assumed to be 65 percent whereas the efficiency of the cracking still was assumed to be 70 percent. These assumptions are both favorable to the cracking processing.

If the following values for the constants are used:

$V_g = 5$	$C_r = 0.63$	$E_s = 0.7$	$S = 0.98$
$V_c = 1.50$	$R_F = 2$	$E_c = 0.93$	etc.
$C_c = 1.0$	$V_f = 0.6$	$C_d = 0.083$	

the profit by coking directly amounts to almost a cent for each gallon of fuel oil that is processed. This large margin indicates clearly that the direct coking of a stock, rather than distilling, cracking, and then coking, is the best method. The use of different constants than those used above will alter the results to some extent but it would be almost impossible to find conditions in which the direct coking operation would not be the more profitable method. The usual argument in favor of distilling, cracking, and then coking, is the larger yield of gasoline that is said to be produced. However, this advantage, if it really exists, is not great enough to overcome the additional handling expenses involved in the additional distillation, etc. In fact, data from modern coking units show that the ultimate yield of gasoline is about the same as the yield obtained when the stock is distilled, cracked, and then coked.

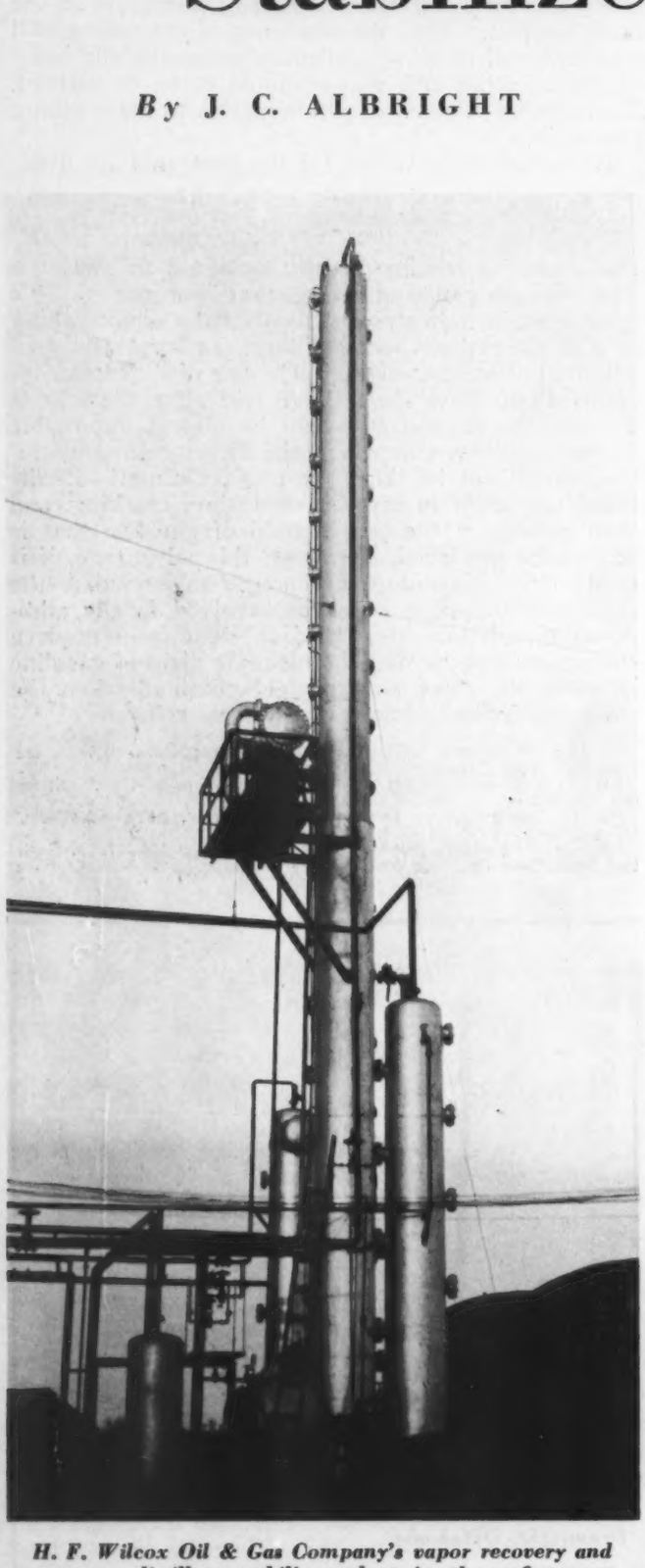
[1] Nelson—"Petroleum Refinery Engineering," pages 476-481, 488, McGraw-Hill Book Company, New York, 1936.
[2] W. T. Ziegenhain, "Tidal Refining Co. . . . Knowles Unit," Oil and Gas Journal, pg. 16, Sept. 10, 1931.
[3] D. G. Jones, "Coking Petroleum Residues . . . Antiknock Fuels," Oil and Gas Journal, pg. 113, Dec. 26, 1935.
[4] Nelson—"Petroleum Refinery Engineering," pg. 316-317, McGraw-Hill Book Company, New York, 1936.



Tide Water Oil Company, Drumright, Oklahoma

Interesting Operating Features In Stabilizer System

By J. C. ALBRIGHT



H. F. Wilcox Oil & Gas Company's vapor recovery and pressure distillate stabilizer plant in the refinery at Bristow, Oklahoma.

H. F. WILCOX OIL & GAS COMPANY recently erected a new pressure-distillate stabilizer and vapor absorber replacing older equipment which had been used for several years. The new pressure-distillate stabilizing plant contains several novel features.

There were a number of features the company desired to eliminate from pressure-distillate fractionation when plans were made for the erection of the new unit. One was to do away with maintenance of a complex system of vapor lines leading from the plant storage tanks, rundown tanks and accumulator drums to the old recovery plant. Another item under consideration was that of obtaining efficient fractionation and stabilization of the pressure distillate, or cracked gasoline, without the necessity of employing a greater number of employees than profits from refinery operation returns would seem to justify.

To bring out the features of the new plant and its simplified operation more forcibly, a short resume of the older type plant seems to be justified. This old plant was located quite a distance from the other units of the refinery, and was operated on the compression principle, which took vapors from all the rundown tanks, storage vessels and accumulator tanks and drums in the straight-run distillation unit and the cracking plant. In order to lessen the load of vapors picked up by this compression plant—which was making about 5000 gallons of recovery gasoline daily—and especially those coming from the accumulator and receiving drums, additional coolers were purchased and installed on all distillate lines leaving the columns and towers at the straight-run plant, the rerun and the cracking plant. These were so arranged that they would function as after-coolers, reducing the temperature of the distillates and also condensing practically all of the lighter ends which were desirable. After these after-coolers were installed and operating, the load on the old compression plant fell to such a low point that instead of making 5000 gallons of gasoline daily, the net production was only about 300 gallons. Obviously, this small amount of recovered gasoline was not sufficient to justify the epense of wages and maintenance of the compression plant when similar products could be purchased at such a low price per gallon.

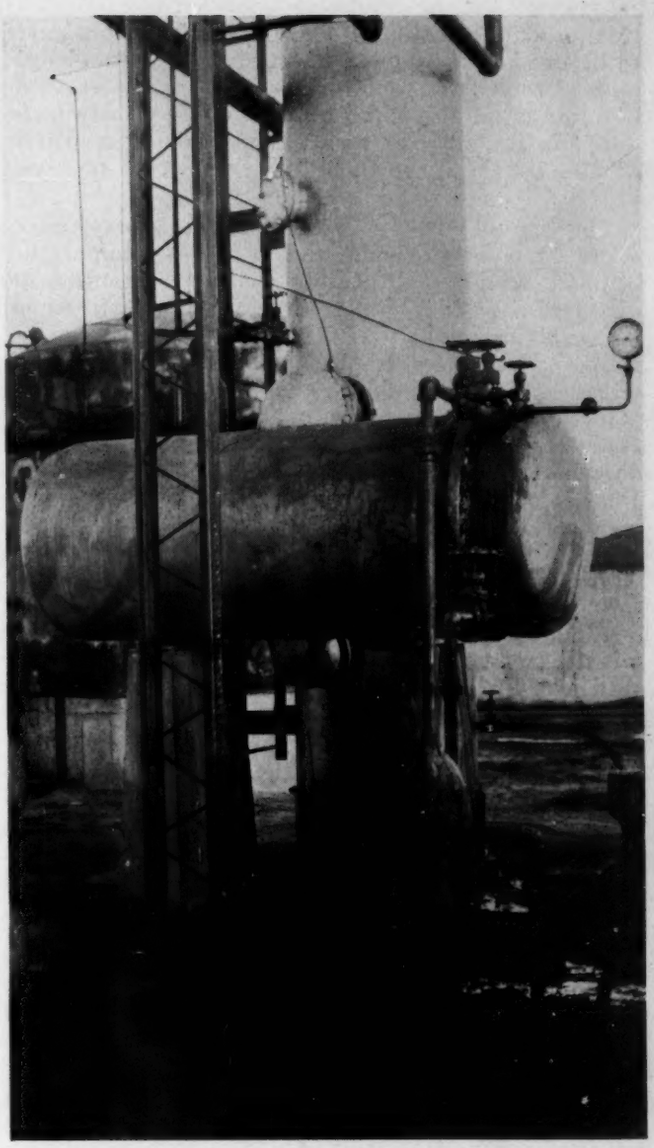
The new unit installed was designed to be self-contained, and by that it is meant that all power required for circulation of gases and liquids was to be obtained from system pressure, and that the oil used to recover the lighter fractions not condensed in the pressure-distillate coolers and condenser boxes was made from the stream of pressure distillate vapors. In order that operating expenses could be pared to the absolute minimum, the plant was built

just outside the cracking plant control-room door where the regular stillmen could observe the operation of this unit as well as the others under their control. Pressure recording and control instruments were attached to the cracking plant control board where they could be easily seen. Flow meters and liquid-level controls, as well as other automatic devices were attached to the plant at all necessary points to make it self operating after it had been placed in equilibrium.

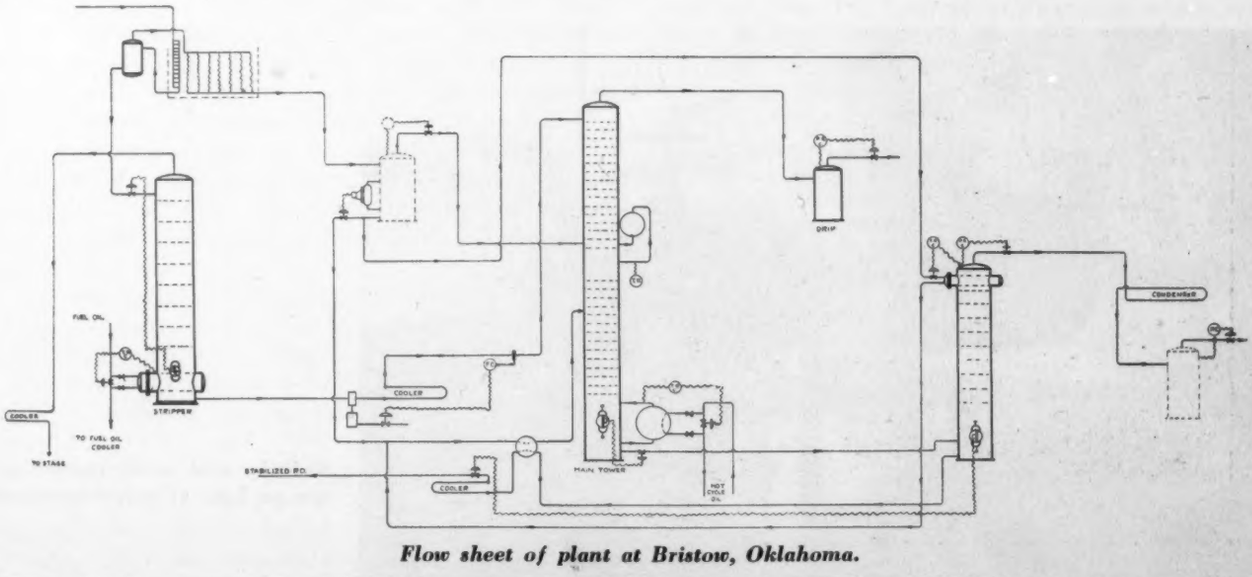
Because of the improved conditions arising from the placing of adequate condensing equipment in the straight-run and rerun units of the refinery, no appreciable loss of vapors is being encountered. Due to this condition, the new plant was designed chiefly to handle only the pressure-distillate production coming from the cracking stills. It reduces a portion of the stream to a stable fraction which will serve as an absorption medium, absorbs the uncondensed vapors and finally fractionates the pressure distillate to any vapor pressure desired. The lighter ends removed from the pressure distillate while in process of fractionation to the desired vapor pressure are also condensed to the required grade to be used as natural gasoline substitute.

The new unit consists of three principal columns, one called the stripper tower, in which the heaviest ends of the pressure distillate is conditioned for use as absorption oil. Another the main column, which is two columns, one superimposed upon the other, and which functions as a stabilizer and absorber at the same time, while the third column is the final fractionator where the pressure-distillate stream is reduced to the required vapor pressure.

In normal operation the hot pressure-distillate vapor stream is passed through a primary condenser made of a small number of vertical condenser sections, where only the heaviest fractions of the stream are liquefied. The entire stream of vapors passes through this condenser section and immediately enters a small pot, or receiving drum where the liquid is separated from the gases. This liquid fraction represents about 15 percent of the total charge to the cracking plant, and is removed directly from this pot



Reboiler section on main column. Small pot in the foreground is the "coke scrubber," for removal of coke from hot oil from cracking plant which is used to heat the reboiler section.



Flow sheet of plant at Bristow, Oklahoma.

to the stripper column. The distillate is considered to be of such a complex mixture of heavy and light hydrocarbons that it is undesirable in this stage to be used as an absorbing oil, and consequently is reduced in the stripper to a product having a gravity of about 34° A. P. I., and an end-point of about 510° F.

The stripper colum is operated at a pressure of about 14 pounds, gauge, and at a base temperature of about 330°F. The heating element to control the distillation of the lighter ends from the stream of heavy oil received from the accumulator pot on the primary condenser is obtained by passing a small stream of hot residuum or fuel oil from the cracking plant through the tubes of the reboiler. This is made an integral part of the column, but with removable heads for inspection and cleaning. The amount of this fuel oil used is controlled by a temperature recorder-controller actuating a diaphragm valve in the hot oil line leading from the reboiler. This valve is placed on a by-pass connection, and the manually operated block valve in the direct line is adjusted by hand at the beginning of a run to permit the passage of a minimum amount of hot oil, insufficient for normal operation, and the instrument valve controlling the overage, or excess hot oil required.

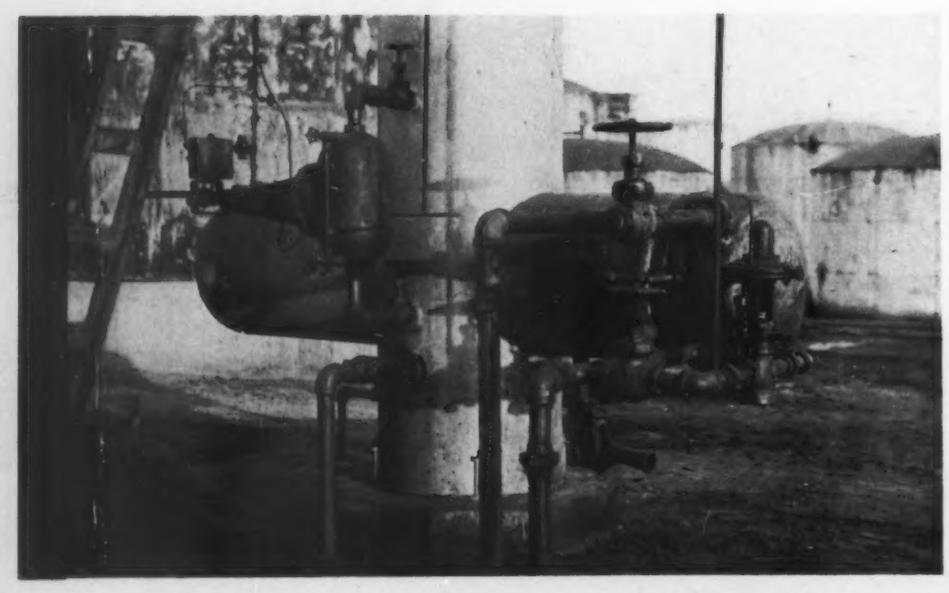
The flow of material from the receiving pot placed at the outlet of the primary condenser is controlled in its travel to the stripper column by a valve in the line leading from the pot to the stripper. A float cage placed on the side of the stripper is controlled by the level of the liquid in the base of the stripper, and in turn the float controls the input of oil to the stripper. If more distillate is received in the distillate pot than is required in the stripper column, it naturally builds up against the action of the valve and flows to the secondary condenser with the uncondensed pressure distillate vapors.

Vapors distilled from the heavy cut processed in the stripper column are removed through an overhead vapor line, condensed and passed to storage without blending with other material at this time. This is carried out in this manner because the fractions removed from the heavy distillate are sufficiently free from sulphur compounds that they can be used for motor fuel without the expense of doctor treating or rerunning with the regular stream of pressure distillate. The overhead stream from the stripper column represents approximately 5 percent of the total charge to the cracking unit, and about one third of the amount of distillate delivered to the stripper. The product of distillation in the stripper has a vapor pressure of about 12 pounds, Reid, and an end point of about 380°F.

The pressure distillate not removed from the stream of vapors through the small accumulator pot is passed immediately through a bank of horizontal condensers placed in a tank above the control room, and are received principally as liquids in the accumulator drum used in previous operations. The liquid line from the base of this drum is split into two separate parts before one passes through a liquid-level control. The line not subject to this control takes a part of the liquid and carries it to the top of the final fractionator for reflux contol. The controlled line permits the remaining portion of the condensate to flow to the lower section of the main column. The stream removed and used in the control section of the final fractionator is returned to and joins the principal portion of the pressure distillate at a point just before admission to a heat exchanger where the bottom cut of the final fractionator exchanges heat with the charge to the lower section of the main column. The unstabilized pressure distillate, after being partially heated in the exchanger is introduced to the lower section of the main column above the tenth plate, counting from the base of the tower.

The conditioned distillate in the base of the stripper column is picked up by a 6x4x6-inch simplex pump with a suction pressure and delivers it while hot with a discharge pressure of 140 pounds, to a cooler and to the top of the upper section of the main column to absorb the uncondensed vapors driven from the pressure distillate in the lower section of this column.

One of the novel features of this plant is in the manner in which the pump is driven. Instead of the usual steam, or electric motor, this pump takes energy from the residue, or stripped gas coming from the top of the main column. A pressure-controlling valve is located on this residue line after the



Reboiler and outlet control system on base of stripper column.

Main column feed to finished pressure distillate exchanger in Wilcox's plant at Bristow.

gas is passed through a drip, or gas scrubber to remove what oil and condensate might be brought over with the gas, and the pump pressure line removes the required volume from a connection between the scrubber and the back-pressure control valve.

As the system pressure placed upon the main column is in the neighborhood of 140 pounds, that is quite sufficient to operate the pump. The exhaust line is tied into this same residue line, but at a point down stream from the back-pressure control valve. This causes the pump to operate under an exhaust back pressure of about 25 pounds. The material leaving the discharge side of the small pump is under about 330°F., and is immediately passed through a cooler section in the condenser box to reduce the temperature sufficiently that the oil will pick up the desired amount of light vapors in the top section of the main column.

The vapors not condensed in the main condenser section through which the stream of pressure distillate passes, and received together with the distillate in the receiving drum, are passed out overhead to the top section of the main column to come in contact with the reduced material pumped to the top of that section from the stripper column by the small gas-pressure-driven reciprocating pump. The operation of the double column is similar to that encountered at other refineries operating this type of equipment, as designed by Burrell-Mase Engineering Company.

The reboiler placed outside the bottom section of the main column receives its heat from a split stream of hot oil from the cracking plant charge pump, and is maintained at about 330°F. This hot stream of cracking material passes through a temperature-controlling valve, and after being used in the reboiler tubes, re-enters the charging pump at the cracking plant. Coke is prevented from entering the tubes of the reboiler by the use of a small pot through which the hot oil must pass, and causing the coke particles to drop to the bottom where it is drawn away through a bleeder valve.

The fractionated, or stabilized pressure distillate after being stripped of its uncondensable gases is removed by system pressure from the base of the main column to the third tower in the series where it is further treated to obtain the desired vapor pressure. Vapors liberated from the pressure distillate in this column passes upward where it meets the cold fresh distillate passing through the tubes of the overhead reflux drum and is reduced to an eight-pound product. Gases removed from the overhead vapor line leading from the top of the third column are treated in a condenser section to liquefy them into natural gasoline substitute. This product corresponds to a 26/70 natural, and is passed by column pressure to storage for treating with doctor and used as a blending agent.

The amount obtained by final condensation of the vapors from the third column represents approximately 4.5 percent of the charge to the cracking plant. The amount of stabilized pressure distillate removed from the base of this column where it receives its final treatment amounts to about 46.5 percent of the charge to the cracking stills.

With all the pressure, temperature and rate of flow controllers functioning, this plant requires very little supervision. The little need for supervision is secured mainly by the use of adequate control instruments, and the fact that it is so near the control room that the stillman on duty need not walk far to observe the operation of the plant. No additional power is required in the operation of pumps to move the gasoline and distillate from one vessel to another because system pressure from the cracking plant is used at every possible point.

Gas passed from the top of the main column represents an average of about 500,000 cubic feet daily, and is used in the cracking operations by burning under the stills and in the boiler plant for fuel. Be the streams are low enough in temperature that very cause of the attention given condensing equipment, little valuable gas is popped to the air.

Continuous Acid Treatment of

Cracked Distillates

J. S. WALTON
Member of Staff, DeFlorez Engineering Co., Incorporated

DECREASE of sulfur content by the use of sulfuric acid is accomplished primarily because of the preferential solubility of sulfur bearing compounds in the acid layer, and secondarily because the heavy complex portions of the cracked distillate usually contain a large amount of sulfur, and these heavy compounds are easily acted upon by the acid with resultant polymerization and removal in the acid layer.

From high-sulfur crudes and cracking stock from these crudes, a deep crack ordinarily will produce a distillate high in sulfur, the sulfur content increasing rapidly with increasing severity of cracking. This behavior of high-sulfur stocks usually limits the percentage of total gasoline obtainable from the crude, for, after the sulfur content of a cracked distillate reaches a certain high point it becomes uneconomic to produce higher yields of gasoline because of excessive treating costs.

Depending on local prices and specifications for gasoline and fuel oil, and on prices of acid, the maximum amount of acid which can economically be used in treating a cracked distillate ranges from 12 to 18 pounds per barrel of cracked distillate. This high amount of acid is only necessary, of course, on distillates from high sulfur-crude such as that from Venezuela. On some very highly cracked distillates an excessive amount of acid also is necessary but of late years the production of these distillates has been decreased in favor of more stable types.

In a straight-run distillate from a high-sulfur crude a high percentage of sulfur exists as mercaptan sulfur. This is not true to such an extent in cracked distillates, so that removal of sulfur content from the latter stock is necessary because of maximum sulfur content specifications rather than because of malodorous properties or corrosive tendencies. Also in the treatment of straight-run distillates, acid is used in order to decrease cost of doctor sweetening whereas with cracked distillates this factor is usually secondary to the removal of sulfur in order to meet the above mentioned maximum sulfur specifications on the finished gasoline.

Since large amounts of acid are necessary on high-sulfur oils, the stability of finished gasolines from these high-sulfur stocks usually is good because unstable and gum-forming compounds have been removed during the process of sulfur reduction. For this reason the technique of acid treatment of a high-sulfur distillate is actually not so difficult as the treatment of a low-sulfur oil which is unstable. In other words the amount of acid required in the latter case is governed by the desired stability of the finished gasoline rather than by the sulfur content. Therefore a greater opportunity exists for acid saving, and for improved technique in the treatment of unstable distillate, than exists in the treatment of high-sulfur oils. This does not necessarily mean that a greater actual reduction in pounds of acid per barrel can be accomplished by improved methods of treating unstable distillates, but the percentage decrease in acid consumption will be greater than in the case of the high-sulfur material.

USE OF INHIBITORS

With the increasing use of inhibitors, the number of alternatives open to the refiner has been enlarged and it is often a difficult problem in economics to decide just what alternative offers the greatest saving in treating and manufacturing costs. For example the refiner may have the opportunity to entirely eliminate acid treatment by decreasing end-points slightly and using an inhibitor. Or it may be possible to inhibit the lightest fraction of the cracked product and acid-treat the heavier cut. Again a combination acid-treat plus a smaller amount of inhibitor may be the best solution. Another factor to be considered is the length of time the finished gasoline is to remain in storage before reaching the consumer.

Whatever the ultimate destiny of the use of inhibitors, necessity for acid treatment of some stocks will undoubtedly remain for some time, and while the time may come when inhibitors are so efficient that they eliminate entirely the necessity for acid treatment, future prospects do not solve the immediate problem of more and more rigorous requirements for the stability of finished gasolines.

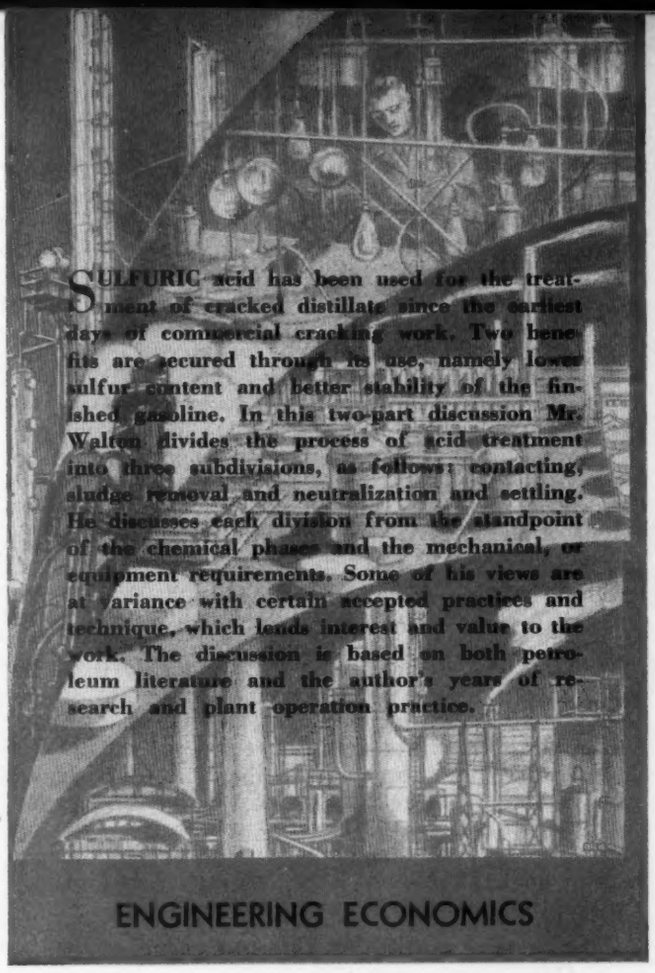
In order to facilitate discussion of the subject, the process of acid treatment has been divided into three subdivisions:

1. Contacting.
2. Sludge removal.
3. Neutralization and settling.

CONTACTING

Earliest acid treatment of cracked distillates was carried out in batch agitators where a quantity of acid was held suspended in the oil layer by an air stream entering the batch agitator near the apex of the cone bottom. This discussion will be limited to continuous treaters, but in passing over batch methods it can be mentioned that they have become obsolete because of

(a) High liquid losses of most desirable fraction of distillate.
(b) Lower barrels capacity per dollar invested.
(c) High cost of repairs and frequency of repair items.
(d) Lack of control of selectivity of reaction, causing a lower quality product and loss of octane value.



SULFURIC acid has been used for the treatment of cracked distillate since the earliest days of commercial cracking work. Two benefits are secured through its use, namely lower sulfur content and better stability of the finished gasoline. In this two-part discussion Mr. Walton divides the process of acid treatment into three subdivisions, as follows: contacting, sludge removal and neutralization and settling. He discusses each division from the standpoint of the chemical phases and the mechanical, or equipment requirements. Some of his views are at variance with certain accepted practices and technique, which lends interest and value to the work. The discussion is based on both petroleum literature and the author's years of research and plant operation practice.

ENGINEERING ECONOMICS

(e) Deleterious effect of oxidizing atmosphere mixed intimately with the distillate.
(f) High acid consumption.
(g) Fire hazard incidental to large quantities of oil present in the treating system at one time. Generation of static electricity caused many fires in systems of this type.

Continuous treaters were first constructed because of the shortcomings of the batch systems, and from the first were found to be far superior to the batch process. Acid regulation was the first operating feature to cause trouble, but treaters soon learned to judge the proper amount of acid to use by "rosy" color of the acid oil. Regulation usually was secured by a controlling valve from a "blow-case," the procedure being to fill the blow-case almost full of acid, then turn full line pressure of air supply on the drum, the valve leading to the mixing line then being cracked enough to provide whatever amount of acid the operator judged to be adequate. Mixers at first took the form of spirals placed concentrically in a line leading to a sludge settling drum, or a system of staggered baffles arranged to force the mixture of acid and oil through a devious route to the settler.

It was found that with this new tool, the continuous treater, less acid was necessary to make the required quality of finished gasoline as compared with the batch process, and that a much greater capacity in barrels per day could be secured with a like investment.

After this step forward, there arose the problems of finding proper strengths of acid, optimum times of contact, best mixing devices, and methods of further reducing acid consumption. Counter-current contacting has been the direct result of investigations directed toward these objectives.

STRENGTH OF ACID

Today as was true of the first continuous treaters, most of the fresh acid used from storage is 92 percent acid (66°). This does not mean however that the fresh acid is always mixed directly with the raw distillate. Many times the 66° acid is blended with a weaker acid or with kerosene sludge which may be up to about 60° Be. gravity. In between the present practice and the first continuous processes was a period when much acid used directly from storage was obtained from acid-recovery plants. Coming from the acid plant the average gravity was about 59° Be. This strength was found to be sufficiently strong for the treatment of most distillates, exceptions being high sulfur naphthas and excessively cracked distillates. Even with the latter a considerable decrease in treating losses was obtained by first contacting with the 59 gravity acid and later using the 92 percent acid. Acid stronger than the 66 gravity caused an excessively high treating loss. Concentration of recovered acid above 59 to 60 Be. was usually impractical, and for this reason use of the 58 to 60 gravity acid was widely practiced.

From experience it was learned that except in the largest refineries or in isolated localities, an acid-recovery plant would not pay for itself, and with later low prices of acid, an acid plant would hardly pay for the cost of operation, to say nothing of paying back the investment. No fixed limit can be set but on the average it will be safe to say that today an acid-recovery plant will not pay in refineries smaller than 35,000 barrels per day crude capacity. Inhibitors have contributed to the scrapping of acid-recovery plants and future prospects for the recovery of spent acid depend upon cheaper methods of recovery being adopted.

As has been stated previously, most of the fresh acid used today is purchased as 66° acid. In some installations, usually small ones, the fresh acid is mixed directly with the raw distillate, the sludge settled and drawn off to be burned or otherwise disposed of. In other cases the fresh acid is first mixed with kerosene sludge or with other weaker acid before being contacted with the distillate undergoing treatment. Another method of treatment, to be discussed later on under sludge recirculation, is to use the fresh acid on a distillate after the oil has previously been contacted with a sludge acid.

TIME OF CONTACT

Considerable material has been published on the proper time of contact of the distillate with acid or acid sludge. Many observers hold to the idea that it is best to separate the oil and acid layer at the earliest possible time in order to prevent sulfonation and re-solution of undesirables in the oil layer. Disregarding other considerations, such as temperature and state of agitation, this position seems untenable to the writer. There is ample laboratory evidence to show that with temperatures held below a certain limit, well defined for each stock, and with good agitation, the longer the time of contact the better the quality of the treated oil and the less acid will be needed for the treat. On the other hand if a deep layer of sludge is allowed to accumulate in a settler, and if the temperature of the sludge layer passes a certain point, then unfavorable reactions certainly occur. Sulfur dioxides are liberated and react with the oil, giving sulfonic esters almost impossible to remove, and which if not removed will cause instability of the finished product. The reaction of acid with a distillate is exothermic and a settling sludge will carry down a quantity of distillate. Insulated from the main body of oil by overlying sludge, the mixture of sludge and oil will react and as the heat of reaction heats the reactants and products, more vigorous action occurs, forming a cumulative effect which eventually causes a disturbance

in the sludge layer and throws the highly sulfonated oil from the sludge layer up into the main body of oil.

Laboratory determinations of permissible treating temperatures and times of contact are easily made and will vary for each type of raw distillate. It can be said, however, that the sludge layer is the main offender and that "pepper" acid suspended in the un-neutralized distillate will do little or no harm unless the temperature of the oil body is fairly high. Accordingly if the sludge layer is held to a minimum depth, and if projections and traps in the settler are eliminated which would catch sludge bodies, then there is little to be feared from the viewpoint of having too long a time of contact in the settler. If these points are watched, then the larger the settler the better.

Minimum times of contact are not so easy to generalize upon as are maximum times. Early continuous treaters had mixing pipes from 5 to 100 feet long for an hourly charge rate of from 50 to 500 barrels per hour distillate. With this variation it can be seen that no hard and fast rule can be made which will secure optimum results. Where fresh 66° acid is injected directly into the distillate and the sludge drawn off directly, the minimum economic time of contact, depending on intimacy of mixing, will range from 30 seconds to 1 minute. For the more modern recirculation treaters to be discussed later, the minimum economic time of contact will probably be of the order of 10 to 20 seconds.

METHODS OF MIXING

From the earliest types of baffled mixing pipes several later types have evolved. One large corporation has standardized upon a series of short nipples with projecting edges welded to each other at right angles. This gives a turbulent flow and a fairly intimate mixing without causing the acid to become dispersed in too fine a state. Pressure drop through this arrangement is high but since the high pressure is exerted upon welded pipe rather than a vessel, the high pressure is objectionable only from a point of view of pumping costs, and some element of danger from the bursting of corroded pipe under high pressure.

Mixing nozzles are another type of agitation which are used to some extent. These usually are made of strips of criss-crossed alloy bars through which the mixture of acid and oil is pumped at high velocity. A very high state of dispersion is obtained with this arrangement and, as will be explained later on, such a system is objectionable in an acid treater because of difficulty of settling and separating.

A third and perhaps best method is a system of jets or injectors which secure the desired mix by pulling acid into the oil stream. With this arrangement it is possible to secure an acid-oil ratio of as high as one to four in the mixture leaving the injector. Jets may be made cheaply of any desired size and can be adjusted to obtain the desired ratio of acid to oil up to the 25 percent mixture noted above.

Mechanical agitators have come into some use in acid treating since development of improved alloys and acid-resisting compounds. These usually consist of a turbine or propeller immersed in the body of liquid and rotated to give required agitation. Blade corrosion of the propellers is held to a minimum by use of compounds such as Bakelite, or some metal alloy. Agitation by this means is very satisfactory in batch systems, but suffers under the disadvantage of necessity for a packing gland when used on continuous systems. This objection is not an insurmountable one, and at low pressures usually existing in a continuous treating system glands have been known to give long service without trouble even in the existing corrosive medium.

All these agitating methods are more or less variable in giving degrees of mixing. It has been stated that a too intimate mixing effect is undesirable. This is because of the fact that when the acid is in a very fine state of dispersion the rate of settling and the degree of freedom from acid secured by a settler is low. In fact with some distillates from a high temperature operation giving excessively unsaturated products, a vigorous contacting with acid will form an acid oil which will never be clarified by settling. Furthermore even when filtered such an acid oil will retain much of its acidity until neutralized by caustic. Upon neutralization the highly esterified oil forms sodium salts of esters which remain in the oil layer and which are partially decomposed upon rerunning, giving rise to corrosion of rerunning equipment and sulfonation and oxidation of the finished overhead product.

Because of the undesirability of a highly dispersed acid, modern designs use large ratios of acid to oil, but eliminate a too vigorous mixing of the two phases in order to circumvent the deleterious action mentioned in the preceding paragraph. Jets or injectors function well in furnishing the large ratios of acid to oil without causing a high dispersion. The effectiveness of a large amount of acid gently agitated with an oil as compared to a smaller acid quantity intimately mixed, can be illustrated satisfactorily by the mass-action principle

$$\text{Raw Distillate} + \text{Fresh Acid} = \text{Treated Distillate} + \text{Sludge Acid}$$

$$\frac{(C_{\text{treated distillate}}) \times (C_{\text{sludge acid}})}{(C_{\text{raw distillate}}) \times (C_{\text{fresh acid}})} = 1/K$$

where K is the extent to which the reaction proceeds. Now if the concentration of the acid be denoted by the amount of exposed surface, it can be seen that a large amount of acid in large droplets will cause the same extent of reaction as a smaller amount of acid in small particles. (Really the advantage is on the side of the large droplets because C_{sludge} is higher in this case, but the illustration is approximately correct.)

These advantages of mild agitation still hold for the smaller ratios of acid to oil providing sufficient time is allowed to compensate for the lower exposed surface when mild agitation is used. Provision of a long time element in any reacting system means, however, that for a given capacity, equipment must be larger which in turn means higher initial costs and more maintenance. In order to surmount this obstacle, and more important, to fully utilize acid content of sludge, recirculation systems were devised and placed in operation. Other reasons why sludge recirculation is advantageous will be discussed in the next section.

RECIRCULATION AND COUNTER CURRENT SYSTEMS

Principles of counter current contacting have long been known to most treaters working on plant operation of batch agitators. Most treaters know that they can secure a better acid treat on naphthas by adding the acid in "dumps" rather than by using an equivalent amount in one portion. This statement has however been subject to some doubts by the earlier technicians notably Bacon and Hamor quoting Schultz[1]. When not pressed for time or when some doubt exists as to the resultant color of the finished oil, the rule is to use the "dump" method. Even "water" acid does a certain amount of treating on the most unstable or most highly colored materials in a raw oil.

In treating cracked distillates the value of counter current methods is apparent for several reasons, among the most important can be listed:

(a) The most active of the unstable molecules are removed by the weakest acid, allowing strong undiluted acid to be added at the last contacting point to remove the most inert of the undesirable constituents. Thus polymerization losses are minimized, and octane number preserved.

(b) Residual acid in the sludge is utilized which is too weak to be used in securing a finished product and which would too greatly dilute fresh acid if the two acids were mixed.

(c) Easily oxidized molecules tend to be mildly treated and extracted into the acid layer rather than vigorously oxidized with the evolution of sulfur dioxide and formation of oil-soluble esters.

Counter-current systems with sludge recirculation have been built with as many as four separate strengths of sludge being used. For the ordinary plant units of this complexity are not necessary though not impractical. Usually, however, one sludge contacting will prove to be sufficient to give good results although two are easily incorporated if enough kerosene sludge is available for use as the middle strength contacting acid. Ordinarily a treat of five pounds of acid per barrel of kerosene from a light crude will produce ample sludge for use as a recirculated acid on the total pressure distillate produced from the crude in the cracking units.

In mixing sludge with raw distillate, jets or injectors again have certain advantages over other types of mixers or transfer agents. Pumps are capable of handling the sludge but there are two important drawbacks to the use of pumps, namely: corrosion, and smooth regulation of acid quantities. Pumps are expensive to install, particularly acid-resistant ones, whereas injectors are cheaply made, and when made of some corrosion resistant alloy will last indefinitely. Solid metal pistons in pumps reduce corrosion troubles but these are inefficient, especially when pumping against heads of pressure. Continuous treater pressures are not high but are high enough to cause some trouble with use of this type pump. More important still is the fact that an ordinary pump gives a more or less intermittent flow, depending on the type pump, and if an intermittent flow exists, some of the distillate undergoing treatment will be contacted with more acid than necessary, and the remainder will pass through the mixing bend practically untouched by acid, unless a very turbulent flow is maintained in the mixer. Extraordinary turbulence has previously been shown to be unwise.

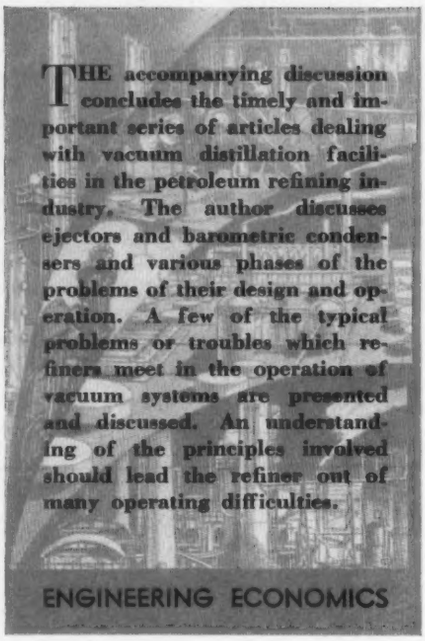
(To be concluded)

Standard Oil Company (Indiana) Wood River, Illinois.

Vacuum Equipment *in the Oil Refinery*

CHARLES T. CHAVE
Alco Products, Inc.

PART II



THE accompanying discussion concludes the timely and important series of articles dealing with vacuum distillation facilities in the petroleum refining industry. The author discusses ejectors and barometric condensers and various phases of the problems of their design and operation. A few of the typical problems or troubles which refiners meet in the operation of vacuum systems are presented and discussed. An understanding of the principles involved should lead the refiner out of many operating difficulties.

THE basic element of a vacuum-producing apparatus is the ejector. A large enough ejector would function without a condenser. The aim in designing all vacuum equipment is to reduce the size of the required ejector to a minimum. The primary purpose of a vacuum condenser is to reduce the condensables in the non-condensable exhaust with as little pressure drop as possible. A direct-contact steam condenser should always be considered in this light, and the absolute pressure at which a system is run should be selected with this in view.

Direct-contact or mixture condensers usually are used for condensing process steam, since very large surface condensers would be required for this work. The countercurrent barometric type of jet condenser is employed, since:

a—The pumping costs are a minimum.

b—The countercurrent principle reduces the required air capacity.

Figure 8 shows two hydraulic arrangements of mixture condensers. Figure 8A shows a low level jet condenser. This type rests directly on the ground and water is pumped from the condenser against atmospheric pressure. The injection water is drawn in by the vacuum. Obviously this pump must work under a head of about 30 feet, depending on the vacuum. Figure 8B shows a barometric condenser. The condenser must be elevated to such as height that the water can discharge from the barometric leg. Water at atmospheric pressure will rise to the height *a*, about 33 feet. The distance from this point to the water inlet represents the pumping head required. This is usually 10-15 feet.

Another striking difference between the two arrangements shown in Figure 8 is the direction of the steam flow. By using a parallel flow arrangement in Figure 8, in which the coldest steam-air mixture meets the hottest water, great advantages in equipment arrangement are obtained when jet condensers are used with steam turbines. This arrangement results, however, in a high degree of saturation of the air leaving the condenser, necessitating an external air cooler for large condensers. With counter-current steam flow, as shown in Figure 8B, the coldest vapor meets the coldest water. When large quantities of non-condensable gas are present in the steam, as is the case for oil-refinery condensers, the counter-current condenser must be used.

The barometric condenser problem looks easy. The average layman believes that steam condenses instantaneously upon contact with water. Unfortunately it does not condense immediately, and this leads to two philosophies of design which really amount to the same thing. One attack is to consider the *time required for the water and steam to be in contact in order for the steam to condense.* Another attack is to consider this as a problem in *surface* heat transfer and to calculate the heat transfer rate and the surface required. If we plot the temperature of water and steam versus the surface, as in Figure 9, we obtain a picture of the problem. Due to the presence of non-condensable gas, the steam and gas mixture drops appreciably in temperature. The value of $(T_{sat} = T_{water\ outlet}) = A$ is known as the "terminal difference." The value of $(T_{gas\ outlet} - T_{water\ inlet}) = B$ is known as the "approach" These two values are important and interdependent. The smaller "A" can be made for a given discharge water temperature, the lower may be the saturated steam temperature and the possible absolute pressure. The smaller "B" can be made, the less the amount of water vapor carried to the primary ejector. These two temperatures are considered, in the trade, as the criteria of the performance of a barometric condenser.

The mean distance between the water and steam temperature lines is the MTD. This is *never* the log MTD. Using the heat transfer concept, the surface of exposed water is $\frac{\text{BTU/hr}}{\text{Um} \times \text{MTD}}$ where Um is the mean over-all heat transfer rate.

In dealing with condensation problems, it is more correct to speak of the mass transfer of the vapor rather than the heat transfer. The over-all heat transfer rate is controlled by:

1—The diffusion of vapor to the water surface.

2—The termal resistance of the water.

Effect number two is controlling for a fairly pure steam, as is to be had in a power condenser. Effect number one is controlling when the amount of non-condensable gas is high.

The rate of diffusion of vapor to the water surface may be expressed as:

K = Pounds per hour per sq. ft. per mm. Hg. partial pressure difference.
Pounds steam condensed per hour = KA × Pm.

A = Water surface.

Pm = Mean difference in partial pressure of steam and partial pressure exerted by water surface.

It can be seen that if the water is hot at the surface and cold in the center of the stream, the mass transfer rate "K" is reduced. This happens when the steam is very pure and the water side rate becomes controlling.

The value of the mass transfer rate at any point in the condenser depends upon:

1—Mass velocity.

2—Hydraulic diameter, or the ratio

$$\frac{\text{Vol. of Container}}{\text{Sq. feet of Surface}}$$

3—Inversely as the partial pressure of the non-condensable gas.

The third effect, the partial pressure of non-condensable gas, is uncontrollable in the design of a barometric. It is often controllable in the design of the process. For example, running cracking-still tar to a vacuum tower without a preliminary flash is illustrative of bad practice in this respect.

Increasing the mass velocity is a practice which often results in a pressure drop in the condenser, partly defeating the purpose of a low approach. However, at the outlet end of the condenser the partial pressure of non-condensable gas is so large that the mass transfer rate becomes very small if only natural convection velocities prevail. Colburn and Hougen give, for an air and steam mixture, the value

$$K = 2.36/Pg$$

At the condenser inlet, Pg may be 1 mm. or less. The controlling resistance is then undoubtedly on the water side. At the outlet, Pg may be 30 mm. or more. It is therefore necessary to follow one of two courses in design:

a—Take a pressure drop, using high vapor velocities, particularly at the cold end of the condenser.

b—Greatly increase the physical proportions and the exposed water surface in the condenser.

The area of the exposed water surface in a condenser depends upon the quantity of water, the extent of subdivision, and the time in the condenser. The problem of design is to favor the maximum exposed water surface and the maximum heat transfer rate.

As a matter of fact, there are three characteristic designs on the market, as illustrated in Figure 10. Type A is typical of a "pressure drop" condenser. It is usually offered with considerably less height and weight and a much better approach guarantee than Type B. When it is overloaded with non-condensables, or with oil vapors, which have the same effect, the pressure drop greatly increases, with oftentimes little change in the gas outlet temperature.

Type B operates with little or no pressure drop. The writer has seen these condensers operate with no noticeable deflection of a kerosene manometer connected between the steam inlet and the air discharge. When they are overloaded, the gas discharge temperature rises, and more condensables are carried to the ejector. The absolute pressure in the system rises due to the increased ejector load. Type B has the disadvantage that the ejector load may increase to the "breaking point" on the characteristic curve of the ejector, and the ejector will cease to function.

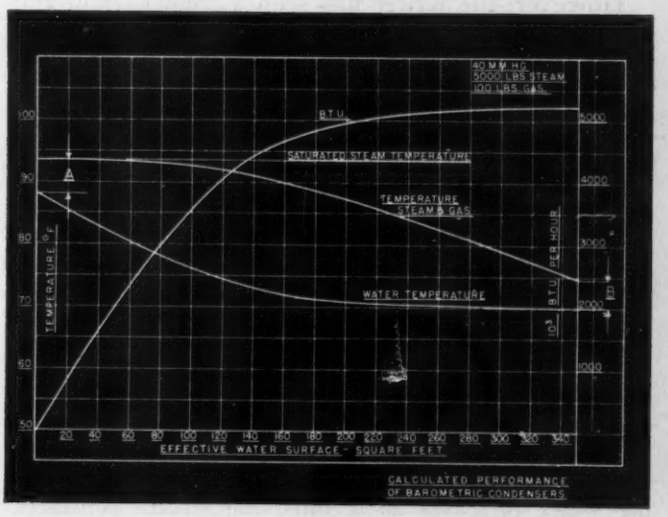


FIGURE 9

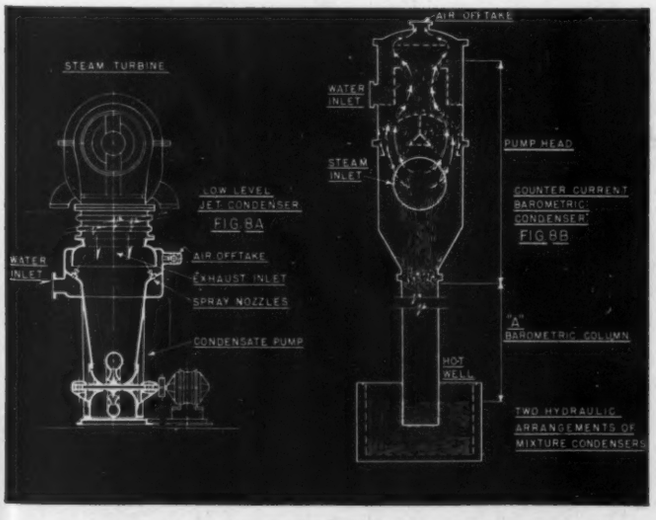


FIGURE 8

On the other hand, an overloaded job can be fixed by the following methods:

a—Add an additional barometric as an external air cooler.

b—Add additional ejectors.

With Type A, it is very likely that the pressure drop will increase due to overloading to a point where additional ejectors or external air coolers will do no good. On the other hand, with Type B it is inherently difficult to get a large water surface per unit of volume, unless a complicated hydraulic arrangement is used. In some designs of this type, a series of slotted trays are so arranged one above the other as to produce a dense rain in the condenser, through which the steam passes. Another device is to use "disk and doughnut" pans with many small holes drilled in the bottom. These condensers give, in theory, very much higher effective water surface

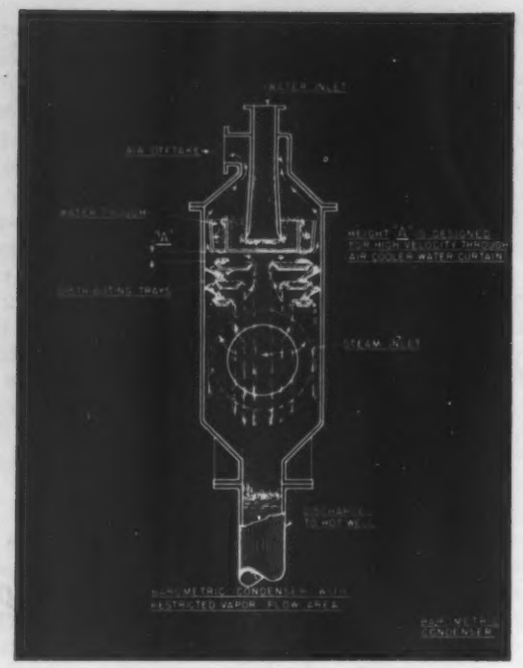


FIGURE 10-A

than most conventional types, but often rapidly plug up with dirt and become ineffective.

However, the writer has seen a condenser of this type in service some months on Mississippi River water, which operated with a terminal difference of 5°F, an approach of less than 1°F, and a pressure drop of less than 1 mm. Hg.

We are at once led to another method of classifying barometrics; i.e., by the method in which the water surface is exposed. Type B, Figure 10, shows the use of umbrellas and circular weirs to give a conical sheet of water. Such sheets must be broken to permit the steam to enter, otherwise they will be unstable. The angle piece (A) in Figure 10-B is a valuable patented feature of this condenser, for it permits the stability of the water curtain.

In Figure 10A we see a series of circular notched weirs which give a rain in the condenser.

All these processes require height in a condenser to give surface. When water is discharged in streams, or in films, as from a weir, the velocity of the water increases as it falls, the stream contracts, and less and less area per foot of height is presented the further it falls. A rain likewise gives less effective surface per foot of height the further it falls, since the drops get further and further apart. Likewise, surface temperature of the droplets is rapidly raised, but due to the lack of turbulence and the low thermal conductivity, the heat does not penetrate toward the center. Hence frequent interruptions of the fall of the water increase the effectiveness of the condenser in two ways: by increasing the exposed water surface, and by causing turbulent mixing at frequent intervals.

The most effective way in which to increase the water surface is to spray the water. This device is used in most power condensers because of the limited space available. It has the disadvantage of considerably increasing the pumping head, and being sensitive to debris in the water.

A spray design using a non-clogging nozzle is shown in Figure 10C. The unique feature of this condenser is that a series of orifices are used to "shave" off a flat sheet of water from the rising jet. The steam passes through the very thin stable high velocity films of water, and good contact is obtained. This condenser operates satisfactorily when out of plumb.

The actual mechanics of condensation may be described as a migration of vapor molecules from a region of high partial pressure existing in the main stream of the gas and vapor mixture, to a region of low partial pressure, existing on the water surface. This transfer of particles is directly proportional to the partial pressure difference existing between these two regions, and not the temperature difference.

The mass transfer rate has been expressed by Colburn and Hougen as follows:

$$K = 80\frac{V^{0.9}F}{Mg^{0.5}Pg}$$

The above is for turbulent flow. In this formula,

V = mass velocity, pounds per second per sq. foot.
Pg = partial pressure of the gas.
Mg = molecular weight of the gas.
F = "entrance factor" for tubular equipment.
$F = 1 + 1.6\ (10^{-0.1N})$ for tubular equipment.
N = ratio of length of tubes to outside diameter.
K = lb/hr × sq. ft. × in. Hg.

For viscous flow, below the critical velocity,

$$Vt = \frac{0.1^{\epsilon}\,(Mg)^{0.6}}{29\,F^{1.25}}$$

$$K = 2.36/Pg$$

Let us now consider a typical problem using these data.

Required to handle in a barometric condenser:

5000 lb/hr steam
100 lb/hr gas, 30 mol weight = 3.33 mols
70 °F. water
40 mm.Hg

1. Outlet water temp. assuming 5°F. "Terminal Difference"
   Saturation temp. at 40 mm. Hg = 93°F.
   Terminal difference = 5°F.
   Outlet water temperature = 88°F.
   Rise in water temperature = 18°F.
2. Heat balance
   BTU/lb steam at 40 mm., saturated = 1101.4
   BTU/lb water at 88°F. = 56.0
   BTU/lb steam condensed 1045.4
   $1045.4 \times 5000 = 5230000$ Heat in steam
   $100 \times (93 - 73) \times 0.50^{*} = 1000$ Heat in gas. Neglect.
3. Water quantity $= \frac{5230000}{18 \times 500} = 580$ GPM or 290000 lbs/hr

   Assume that we have an initial velocity of 25 feet/second.

   At 93°F, we have $\frac{359}{18} \times \frac{760}{40} \times \frac{460+93}{492} = 426$ cu ft/lb

   Mass velocity is then $\frac{25}{426} = 0.0582$. This corresponds to a flow area of 23.7 sq. ft., or 5'-6" diameter.

   Assuming water streams ¼" dia. x 1' long as "tubes",

   $F = 1 + 1.6\ (10^{-0.1 \times 48})$, or F = 1.53.

   Since F approaches a low value of 1, assume 1.50 as a likely value.

$$Vt. = 0.1\frac{(Mg)^{0.6}}{(29)\,F^{1.25}} = 0.1 \times \frac{(30)^{0.6}}{(29)} \times \frac{1}{1.50}\,1.25 = 0.0587$$

   Hence we have viscous flow condition as soon as condensation sets in.
4. First 60 percent of condensing. Tabulation by zones of equal heat transferred.

A total of 345.8 sq. ft. of surface is required, on the basis of a velocity below turbulent flow all the way through the condenser.

The terminal "MTD" is 5°F. Based on this,

$$U = \frac{5230000}{345.8 \times 5} = 3030$$

This transfer rate for steam to water is decidedly in line with expectations.

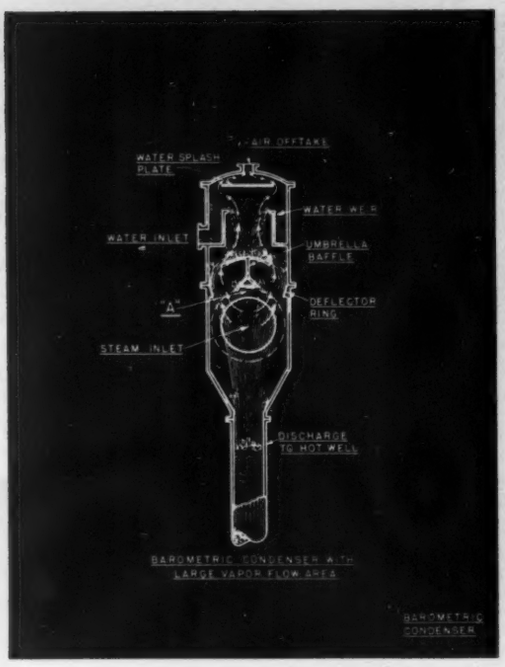


FIGURE 10-B

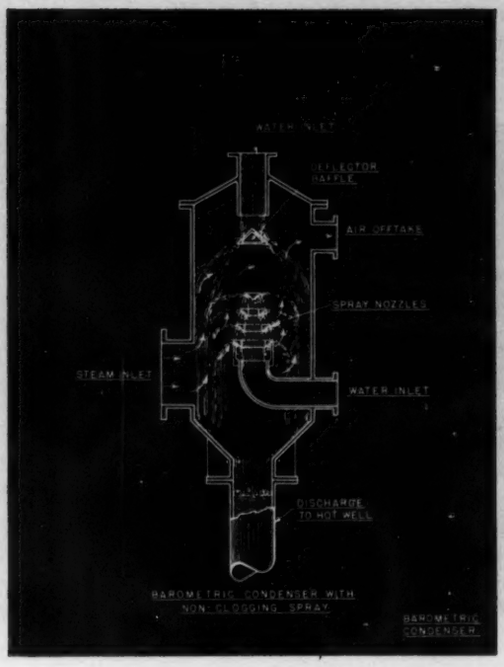


FIGURE 10-C

In order to design for 345.8 square feet of surface, we need a circular curtain, averaging 4 feet in diameter, falling about 14 feet. Both sides are effective. With a condenser 5-6-inches in diameter, we get a job 5½ feet by 16 feet high, which is quite in line with a commercial size. A number of cascades, say 2-3 feet apart are required to mix water up and prevent contraction of the curtain.

Assuming we had turbulent flow in the air cooling section, say 100 feet/sec. velocity, or 0.235 pounds per second per square foot,

$$K = 80\frac{V^{0.8}F}{Mg^{0.8}Pg} = \frac{80 \times 0.313 \times 1.50}{5.48} = \frac{6.89}{Pg}$$

The surface of zones 6 to 9, totaling 169 square feet, could now be cut to $137.7 \times \frac{2.36}{6.89} = 47.7$ square feet.

Referring to Figure 10-A, in which the saturated gas is caused to pass through a short curtain of water at a high velocity, we could, perhaps, get an even better reduction in the total size of the condenser by this practice. The heat transfer at this point may be determined only by empirical means. On the other hand, a design of this character is not suitable for high overloads. If non-condensable gas, superheated steam and a large proportion of oil vapors enter the condenser, the diffusion rate in the lower section is greatly reduced. As a result, large volumes of steam try to pass through the small openings with a very high pressure drop.

The basis of design given above is perhaps pure conjecture. This design calls for about 350 square feet. This is a condensing rate of 14 pounds per hour per square foot. The volume is 380 cubic feet. This is 13.2

TABLE 4

First 60 percent of condensing. Tabulation by zones of equal heat transfer

Zone	1	2	3
Btu/hr	1,040,000	1,040,000	1,040,000
Lbs./hr. condensed	1,000	1,000	1,000
Lbs./hr. flowing	4,500	3,500	2,500
Mols flowing (steam)	250	194	139
Mols of gas and steam	253.3	197.3	142.3
Partial pressure of steam, mm.	39.6	39.3	39
Partial pressure of gas, mm.	0.527	0.675	0.931
Temperature of steam	93	93	93
Temperature of water (mean)	86.2	82.6	79
Mass Transfer, K	4.47	3.5	2.52
Vapor pressure of water, mm.	32	28.5	25.2
Partial pressure diff., mm	7.6	10.8	13.8
Lbs. per hour x square foot	34.0	37.8	34.8
Square feet required	29.4	26.5	28.7

$K = 2.36/Pg$.

TABLE 5

Last 40 percent of condensing. Tabulation by zones of temperature drop.

ZONE	4	5	6	7	8	9
Temperature, ° F	93–90	90–87	87–84	84–81	81–78	78–75
Vapor pressure steam at low temperature	36	32.8	29.8	27.0	24.6	22.1
Percent of total pressure	90%	82%	74.5%	67.5%	61.5%	55.2%
Mols/hour steam at low temperature	30	15.1	9.76	6.90	5.33	4.10
Pounds/hour steam	2,000–540	540–272	272–176	176–124	124–95.8	8–73.9
Pounds/hour condensed	1,460	268	96	52	28.2	21.9
Btu/hour	1,590,000	295,000	106,000	57,300	31,000	24,000
Temperature water	77.2	71.7	70.7	70.3	70.1	70.1–70
Pounds/hour steam, mean	1,270	406	224	150	110	85
Mols, mean (steam)	70.5	22.6	12.4	8.33	6.10	4.72
Mols, total	73.83	25.93	15.73	11.66	9.43	8.05
Pg, mean, mm	1.8	5.13	8.45	11.4	14.1	16.5
K	1.31	0.460	0.279	0.207	0.167	0.143
Vapor pressure water, mm	21.7	20	19	18.8	18.8	18.8
Partial pressure diff., mm	14.3	12.8	10.8	8.2	5.8	3.3
Pounds/hour per square feet	18.7	5.9	3.1	1.7	0.97	0.472
Square feet required	78.0	45.3	31.5	30.6	29.1	46.5
MTD	17° F.	16.8° F.	14.8° F.	12.2° F.	9.4° F.	6.5° F
Btu/hour per square feet per ° F	1,200	386	226	154	110	79.3

pounds of steam per cubic foot. The writer has seen a condenser of the same general design, condensing exactly 20 pounds per "theoretical square foot". The volume rate was nearer 75 pounds per cubic foot. As a

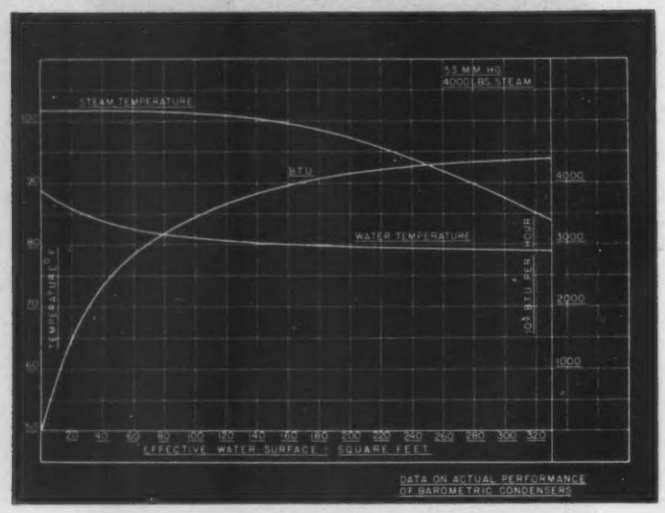


FIGURE 11

consequence, the "terminal difference" and the "approach" were not as good as predicted herein, since the surface was not all effective.

The following table gives commercial practice in design for a "non-pressue drop" condenser, with much better effective water surface than usual.

Type of Condenser	Pounds Steam/Hour x Cubic Feet	Approach	Terminal Difference
As per Fig. 13-B	13.82	5° F.	7° F.
As per Fig. 13-B	12.8	....	....
As per Fig. 13-A	18.2	5° F.	9° F.
As per Fig. 14	46.7	3° F.	4° F.
Spray type, with multiple nozzles	34.6	5° F.	8° F.

Additional data are submitted to show the bids submitted to cover one definite performance requirements:

Ratio steam to dry gas, by weight, at inlet 16.1
Injection water temperature 68°F.
Absolute pressure = 33 mm.

The effect of the method of water distribution on the physical size of the condenser is great. A lesser effect on the price is to be observed, since the spray nozzles are inherently expensive.

Figures 9, 11 and 12 show the comparison of the proposed design and an actual commercial installa-

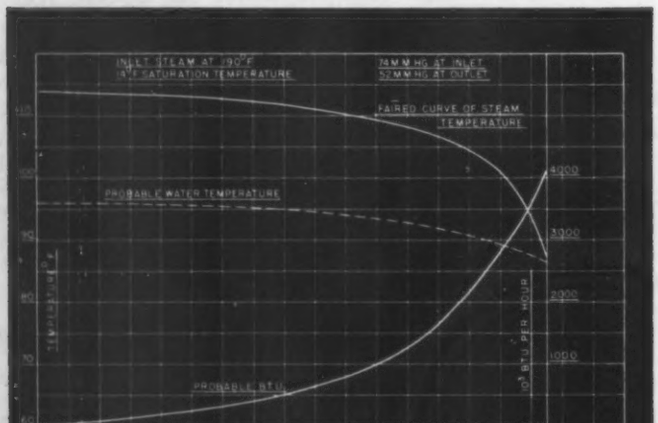


FIGURE 12

tion tested by the writer. It may be seen in Figure 9, derived from the theoretical design, and Figure 11, that there is normally heavy condensation of steam in the bottom of the condenser. Comparison of temperature gradients indicates this clearly. In Figure 12 is shown the performance of the commercial unit when light oil was entering the condenser with the steam. Practically no condensation occurs in the lower section. In the air-cooler section the steam velocity was so great that 25 mm. pressure drop occurred. When handling a normal amount of gas, this condenser operated with no pressure drop. The abscissae of these charts are multiplied by a factor to prevent identification of the actual data source.

From these observations it would appear that no commercial barometric condenser is entirely satisfactory. A design utilizing sheets of water in the lower

FIGURE 13

section, where heavy condensation occurs, and using a spray in the air-cooler section might prove more satisfactory. The pressure drop in the air-cooler section would be eliminated, and a low heat-transfer rate could be overcome by means of a large exposed surface. It has been claimed that, in a heavy-duty condensing zone, fine spray tends to partially evaporate due to the low conductivity of small droplets, resulting in instability of operation. The low amount of heat absorbed in the air-cooler section would make this a matter of no concern. In the lower section of the condenser, stable sheets of water, remixed at proper intervals, would absorb the bulk of the heat.

It is natural that such an undeveloped subject should make trouble shooting a difficult matter. An understanding of the principles involved will lead the refiner out of many operating difficulties. The writer has from time to time investigated complaints from refinery operators concerning vacuum equipment. A few of these typical troubles are discussed in order to show the application of these principles:

1.—*Oil in the discharge water.* This often is blamed on mechanical entrainment. As a matter of fact, it is due usually to saturation of the steam with the overhead product. In a tubular condenser equilibrium condensation does not occur. The oil is sub-cooled 30° to 70°F. below the temperature of the steam leaving the tubular unit. If the oil temperature is brought low enough to eliminate oil "carry over" to the barometric, it frequently results in the condensation of steam in the oil. On the other hand, if the oil temperature is raised high enough to eliminate

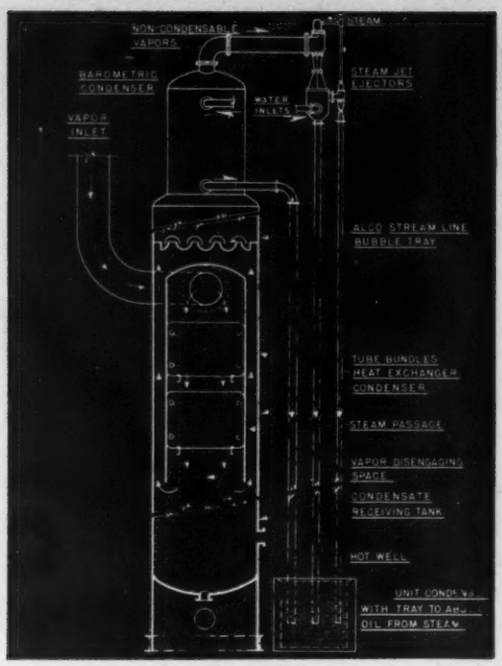


FIGURE 14

water in the product, the steam becomes hot enough to take up considerable oil in saturation. Figure 13 illustrates the mechanics of condensation. The resistant films are shown. It is possible, if saturation temperature of the steam is 90°F., for some steam to condense from the vapor-gas film, even though the main body is only cooled to 160°F. Cold water intensifies this effect. In design, a large tubular condenser designed for warm water, and operating in a low "MTD" will reduce this effect.

In practice, it is always necessary to choose between the two evils, (provided that the surface condenser is large enough, to begin with). With a light gas oil, it is better to condense water in the oil, since separation is not difficult. With a cracked gas oil, 12°-15° API, distilled from cracking-still tar, it is better to keep the product dry, since separation is impossible. If the barometric water is recirculated over a cooling tower, the oil in the water is rapidly concentrated until it reaches nuisance proportions. The writer has found that a highly alkaline water forms an emulsion with the oil which floats, and that if this emulsion is continuously skimmed the nuisance is greatly reduced. The emulsion formed must be properly disposed of: i.e., either broken by long time settling is a heated tank, or burned. It will not be caught by an oil trap, and should not be put in the sewer system.

Figure 14 shows a special feature (patent applied for) a new type of unit condenser. Oil is circulated over a bubble tray, and steam, on the way to the barometric, is passed through it. This cold oil acts as an absorbing and condensing agent, reducing entrained and saturated oil in the steam, as well as superheat. This device, used in replacement of baffles and other schemes has proven beneficial on several installations.

2. *Hunting of the ejectors.* It is a common fault of many operators to use too much inter-condenser water and flood the secondary stage. About 15°-20° rise should be taken on this water.

Overloading will also cause serious hunting. The system should be examined for the following causes of overloading:

a. Leaks.
b. Unusually high still temperature.
c. Low initial on the overhead product.
d. High air content of the condenser injection water.

3. *Sudden loss of vacuum.* The most usual cause of this is a drop in steam pressure. The effects of this on ejector performance have been described above.

4. *Gradual reduction of vacuum, over a period of several months.* Dirt in the nozzles and steam strainers is the usual cause. The writer has known this to happen due to corrosion of the ejectors with some crudes. The throats and nozzles, if removable, must be renewed. Alloys of nickel-cast iron or nickel-chrome steel have done well in this service.

5. *Little improvement in vacuum due to increased circulating water or lower temperature circulating* water. The ejectors control the vacuum. Referring to Figure 7, it may be seen that there is a "dead shut off" point, below which the ejectors cannot maintain the absolute pressure. Hence, in a system designed to run at 45 mm., for example, water double the amount of circulating water might not reduce the absolute pressure to below 40 mm. This fact becomes more pronounced when the ejectors fail to function properly. Even freezing water might fail to give 25 mm. absolute pressure, although the possible absolute pressure is below 10 mm.

The problems of the refinery, and the conditions of operation are so widely different from the steam power plant, that the power condenser is not suitable for this work. So few manufacturers of this equipment have actual oil refinery experience that it behooves the designer, the operator and the purchaser to think for themselves when it comes to equipment of this type. The cheapest is seldom the most desirable.

ACKNOWLEDGMENT

Thanks are due for the constructive criticism of Mr. Carey of M. W. Kellogg Company, Mr. Throckmorton of Alco Products, Inc.; for the assistance of Mr. Forncrook of the Elliott Company, and for the valuable work of Mr. Hunt of Alco Products, Inc., in illustrating this article.

EDITOR'S NOTE: Attention has been called to the fact that the first sentence, fourth paragraph, right hand column, page 49, February issue of THE REFINER, Part 1 of this series, is not clear. The sentence should read as follows: "From 25 to 60 pounds per hour of 30 mol. wt. gas per thousand barrels of feed per day should be allowed in rating ejectors for vacuum stills."

Experimental and Process Development Methods *for Petroleum Oils*

PART II

L. C. TRESCOTT

THE second stage of a semi-scale operation is likely to be an acid treat. It is common claim that it is impossible to duplicate in the laboratory the acid treating results of the plant. If this be the case in any particular instance it can be laid at the door of a lack of real knowledge of acid treating and of plant methods. An experienced treater most certainly can duplicate plant quality and plant yields. Any differences in the two scales will come in differences in procedure. Real experience will tell the treater what allowances to make. More than anything else the laboratory treats give an advance "taste" of the troubles which may be expected. Acid treating is still far from being a science. Many term it a collection of tricks coming out of plant practice.

In making semi-scale acid treats almost any sort of container may be used but for everything up to three gallons the glass percolators of the drug industry are hard to beat. These are tall, narrow, conical vessels of fairly thick glass and provided with a neck at the bottom. As a rule this is closed with corks placed both inside and out. The neck is too small to be of any value in drawing the sludge. It is better to stopper it completely and pour the sour oil off the top of the sludge. The agitation is carried out through an air jet through a glass tube dropped to the bottom.

Some operators attempt to carry on their agitation by mechanical means. This is a mistake unless the plant process also has mechanical agitation. The type of agitation is almost certain to have a considerable effect on the character of the acid sludge. The rolling contact between the acid and the oil in an air-agitated batch produces a sludge different from that formed by the beating action of a mechanical agitator. A certain quantity of air also sticks with the sludge and influences its settling and its flowing qualities. On most experimental acid treats it is best to use air agitation. This is not an argument for one type of agitation as against another. It is just a statement in keeping with things as they are.

One reason why so many treating procedures fail to give results which may be duplicated in the plant lies in the slipshod methods by which such treats are carried out. There is a tendency among the pundits to look on acid treating as a rough proposition wholly lacking the refinements of a truly scientific operation. So they put the acid and the oil together, slosh them around a bit and then try to draw conclusions from the alleged results. Naturally in any line of investigation there may be many small trial shots taken which do not warrant the trouble of close measurement, but the final runs, the ones from which data are taken should be carefully handled and should be balanced as was the distillation end of the job. The oil should be weighed in and out of each stage and its volume should be calculated. Possibly the best way to show this procedure is to give an example.

Let us make this a treat of approximately 10 liters and carry it out in one of the glass percolators, which for our purpose is the agitator. The first step is to weigh this agitator. The oil is then poured in, the weight of the oil plus the agitator is found, the gravity of the oil is taken and the volume calculated. From this volume we calculate the acid necessary. If the results are to be extremely accurate the weight of this acid also is taken but its volume is not calculated. The weight is used as a part of the total weight as a check on the general accuracy of the work.

The air should be started and the temperature of the oil taken before the acid is put in. The temperature should also be taken at the end of the treat in order that there may be a record of the temperature rise. This is usually not a matter of any great importance except perhaps in the case of white oils or oils on which heavy dumps of acid are used. With such treats it is necessary to keep a close watch on the temperature.

The acid should be added slowly. On this point lies one of the big differences between the plant and the laboratory. The plant acid is pumped on over a considerably longer period than is used in adding the acid in a laboratory treat. With the average treat this point probably makes little difference as the amount of acid added is not sufficient to cause any large rise in temperature, but on heavier treats the addition of the acid must be spread over a longer time.

The first dump of acid is usually a "cutter," a dump of about one pound of acid per barrel. This is used to take any traces of water out of the oil. This dump is blown for approximately 20 minutes and then settled an hour. The sour oil is then poured off carefully into another weighed agitator, its weight found and its volume calculated. Any oil and sludge remaining in the first agitator are cleaned out into a graduate and the sludge allowed to settle, after which the oil on the sludge is allowed for. If this is not done the acid treating losses will be unduly large and variable.

On succeeding dumps the same general procedure

is followed. Here, however, we must begin to watch the sludge, note how it pulls together, whether any pepper is left in the oil, and after the sour oil is poured off, whether the sludge carries too much entrained oil and whether it is likely to freeze in the agitator.

When the batch is to be water settled this is done on the last dump. When the agitation time is almost finished and before the air is shut off small portions of water are added and allowed to blow a minute. A few drops of the agitating mix spread out on a glass plate or on a white paper will show the gradual flocculation of the sludge. The oil clears, grows just a bit hazy, and the sludge pulls together in flocs which experience indicates will settle. Then the agitation is shut off and the mix allowed to stand. In the laboratory this final settlement may be overnight. In the plant the settling time is likely to be shorter. Keep this in mind.

In water settling care must be taken not to add too much water. This will result in a hard granular sludge which carries a large amount of entrained oil when it settles, or it may even make the sludge quick setting and cause it to freeze in the bottom of the agitator. The proper flocculation is smooth and of such a nature that the sludge will pull together as a fluid tar. Too much water also breaks up a part of the sludge which goes into the sour oil and aids in the formation of emulsions. The agitation during the settling period must not be too violent or it may put some of the sludge back in suspension. Usually not more than ¾ 0.75 percent of water should be used for settling.

Here again is emphasized the fact that the condition of the sludge after each dump should be carefully noted. Failure to pay sufficient attention to sludges is a frequent cause of trouble when the treat goes to the plant. Remember this—the sludge must flow with reasonable freedom if it is to be drawn from a plant agitator. With a bad test batch you can pour the mess down the sewer or even ditch agitator and all and start over again, but if a batch freezes in a plant agitator it can only be dug out by hand or steamed out.

The sludge should flow as a clean oil-free streak and not as a stringy, spongy mass. The latter is often the result of the use of too much water in settling and while it can be drawn from the agitator it will also carry good oil with it.

When experimental treats are handled in metal agitators the weight of the agitator is not taken. The oil is weighed into it from another container by the method described in charging a still. When process work gets beyond the stage where it can be handled in glass then cans of the narrow-mouthed milk can type such as are used on oil trucks make convenient "tank farms" for the experiment. These are easily handled and cleaned and have tops which protect the samples. They can be purchased in any size from 1 to 20 gallons.

The procedure is the same in the metal agitators as has been described for glass with the exception that the sludge is drawn through a cock at the bottom instead of being allowed to set. And don't forget that the drawing of the sludge, and the observance of its qualities as it flows is one of the important items of treating procedure. The sludge that is drawn should be allowed to settle and any oil on it measured and accounted for.

Acid sludge is not always easy to clean from agitators, particularly if it has been allowed to set. If the vessel is cleaned at once hot water and soap powder will usually turn the trick. The harder sludge can be removed with a mixture of benzol and alcohol.

Now the oil is treated and settled. We have the clean sour oil and the acid sludge. How about yield figures?

Following are the results of a treat on a heavy coastal red oil. The acid was put on in two dumps, one of 7 pounds and a second of 14 pounds per barrel. No cutter dump was used.

First Dump.

Wt. of agitator and oil	13,970 Gr.	Grav. 18.2°A.P.I.
Wt. of agitator and oil	4,600 Gr.	
	9,370 Gr.	9,913 cc.

After Treating First Dump.

Wt. of agitator and sour oil	13,424 Gr.	Grav. 18.6°A.P.I.
Wt. of agitator	4,578 Gr.	
Wt. sour oil	8,846 Gr.	9,348 cc.
Oil on sludge		430 cc.
Total sour oil		9,814 cc.

Stock charged	9,913 cc.
Sour oil	9,814 cc.
Treat loss	99 cc.
Treat loss percent	1%
Yield	99.0%

Second Dump.

Charge 9,384 cc. Represents 99.0% on original raw stock.

Sour Oil from Second Dump.

Wt. of oil and agitator	12,460 Gr.	Grav. 18.7°A.P.I.
Wt. of agitator	4,595 Gr.	
Wt. sour oil	7,865 Gr.	8,348 cc.
Oil on sludge		120 cc.
Total sour oil		8,468 cc.

Sour oil from first dump	9,384 cc.
Sour oil from second dump	8,468 cc.
Treat loss	916 cc.
Treat loss percent	9.8%

9.8% of 99.0% 9.7% loss on second dump.
1.0% loss on first dump.

10.7% Total loss on raw stock.

In making a check balance for extremely accurate work the total weight of acid and oil used may be compared with the total weight of sour oil and sludge at the end of the treat. This will bring out any undue handling losses but as a rule is an unnecessary refinement.

In many cases it is the practice to draw off the sludge and not make any measurements until the final sour oil is reached. This throws pouring losses, etc. into the treating loss.

It may not be considered worth while to take into account the oil remaining on the sludge. Here we must remember that for a normal treat the plant settlement is more complete than is the settlement on a small experimental job. It will be found to be a fair and accurate practice to take this oil into account. In some cases, too, it is not desired to pull the sour oil too close to the sludge. If the oil on the sludge be measured and accounted for the drawing may be done in any manner the operator pleases.

It is also sometimes the custom to figure the acid on all dumps on the basis of the oil charged in the beginning. In view of the fact that there are certain to be some handling losses it is safer to figure the acid for each dump on the basis of the oil actually in the agitator on that dump.

There is every advantage in figuring and balancing

each stage of the treatment by itself. Not only does this practice free the yield figures from hazy complications but it often locates unexpected losses and it will definitely place all losses so that it is easy to determine whether or not they are legitimate.

In this article the matter of sludge control is not touched on, it having been discussed in a previous number. (REFINER, Vol. 13, No. 5, May, 1934.)

NEUTRALIZATION

In general there are two ways of getting rid of the acid in a sour oil. It may be neutralized with alkali and the resulting soaps washed out with water, or fine clay may be put into the sour oil and the acid removed at the same time the oil is decolorized by contact treating methods.

If the sour oil is to be neutralized with soda it should be given a "pepper" blow before the alkali is put in. This is done after the sour oil has been poured from the sludge. The batch is blown with air for a period of one half to one hour. SO_2 is driven off and a coating of sludge will form on the sides of the agitator. Before neutralization the air-blown oil should be transferred to a clean agitator as the neutralization of this sludge is likely to cause trouble. If the sour oil is to be contact treated then the pepper blow is not necessary.

There is probably no point in petroleum technology which requires a larger bag of tricks or more intuition and judgment than the neutralization and washing of sour acid-treated oils and the handling of emulsions. These are also points on which many men attempting development work really know little or nothing. The development of a bag of tricks is just as important to the experimenter as it is to the plant man. Many things are hard to explain but they do work. If enough little stunts that turn the trick are collected and used there does come a glimmer of understanding as to their application, though on this point we have far to go.

Probably the greatest causes of differences between laboratory and plant neutralizations lies in the difference in rate at which the soda solution is put on. The effects of this are most marked when weak soda solution is used. The addition of soda to a large plant batch may take from 30 minutes to one hour. In the laboratory the soda may be all dumped on at once or at most will take less than 10 minutes.

In the plant we begin our neutralization with a large excess of sour oil in proportion to the soda required to neutralize it. As a result acid emulsions are formed in these early stages which may not only be hard to break but at best hinder the total neutralization of the acid. It is a common thing to leave a batch of oil strongly alkaline and come back an hour later to find it just as strongly acid. Had steam been put in in the meantime an emulsion would surely have resulted.

There are several ways in which to overcome this difficulty. First, the soda strength. It is better not to let it be too weak. For well established treats it may be safe enough to use 2° to 5° Be. soda, but for experimental work it is safer to use 10° to 15°.

In the laboratory it is just as well not to try to duplicate any set plant procedure. There is much more to the neutralization of a sour oil than just going through a performance. The main thing is to get the oil actually neutralized. And this does not mean maybe.

Once the oil has been pepper blown a sample should be titrated with phenolphtalein and soda solution of the strength that is to be used for the neutralization. The titration is carried out in a solution of a 50/50 mixture of benzol and alcohol. This mixture prevents the formation of acid emulsions which slow down the action of the soda. Alcohol alone will not do this. From this titration the amount of soda necessary to neutralize the batch is determined and should be added *all at once*. An additional 10 percent will make things safe. The only way such a procedure can be duplicated in the plant is where the soda is added in the pump during the transfer between the treating and the neutralizing agitators. This, incidentally, is the best way to do the job.

On the laboratory job, once the soda is in, the batch should be air-blown until there is no possibility of its going acid. Titrations with phenolphtalein in the benzol and alcohol solution will show this. Additional soda may be added as necessary, and the batch should be quite definitely on the alkaline side.

Up to this stage the neutralization has been conducted at room temperature. When the oil is neutralized it may be steamed at once or if it be a heavy oil which has been highly treated or any treat from which trouble is to be expected the agitator may be left in the hot room over night to allow the heaviest soaps to settle out.

For steaming, the neutralized oils should be transferred to a large balloon flask or other thin container. The thick glass percolators are not particularly suited to steaming. A small portion of water, say 10 percent, is added and the batch is steamed until a break occurs. After this the batch is put in the hot room and allowed to settle.

For trial shots, where yields are not taken a large batch may be neutralized and then split up for steaming. Where yields are taken the sour oil should be weighed in, neutralized and washed, then the neutralized oil weighed out. From the calculated volumes the washing loss may be determined.

In breaking emulsions there are no set rules to follow. The best safety scheme is to reserve a portion of the sour oil, then add a considerable excess of soda and use the sour oil as a breaking agent.

In cases where it is reasonably certain that there will be trouble, about 75 percent of the sour oil may be neutralized with the soda necessary for the whole batch. When this has been thoroughly blown in, the remainder of the sour oil is added. This is better than an acid break as it does not throw the finished oil off test. Many times when the oil is reneutralized following an acid break the worst kind of an emulsion results, due to the presence of acid salts.

In cases where trouble is expected it is wise to keep the water proportion as low as possible. This means the use of stronger soda. If soda solution running from 10° to 15° Be. is used, if every effort is made to have the batch not only fully neutralized but slightly alkaline before it is heated and steam is put in, most acid treats will give little trouble. The base of the whole treatment is to prevent the formation of acid emulsions during the early stage of the neutralization. This means that there must be sufficient soda present of sufficient strength to carry the batch directly to an alkaline emulsion.

It is a fact that the stronger soda usually must be followed by a wash with water, while a weak soda may clean up thoroughly on a first break. On easy treats the latter may be used, but if there is the least chance of trouble it is wiser to go to the stronger soda.

In studying the neutralization of an oil it is usually well to split up a trial batch of sour oil and work it out in several different ways. Try throwing it into an emulsion so that you will know what to expect in that line. The more trouble that can be located at this stage of the game the better are the chances for the treat when it reaches the plant. For other details on the handling of

emulsions refer to a previous article. (Emulsions—REFINER, Vol. 13, No. 4, April, 1934.)

CONTACT TREATING

The final operation on nearly every lubricating oil is a decolorization by means of some sort of clay. Formerly this was done entirely by the percolation method where the oil is allowed to seep through a bed of coarse fullers earth. Later the use of fine clays or the so-called "contact" processes came in. The percolation operation is well established and the methods fixed at least as far as practical work is concerned. Contact processes, however, are still somewhat in the development stage and there is room for much research and investigation along this line.

An investigation possibly may begin by running a color—clay percentage curve on the oil. Here various percentages by weight of the clay are tried on a series of oil samples. The colors are plotted against the percentage by weight on ordinary cross-section paper. The logarithmic curve is sometimes used and may sound more scientific, but its form does not differ greatly from the ordinary curve. A contraction of a part of the logarithmic curve does not add to its clarity, and for practical development purposes it is better to stick to the simpler form.

There is no really standardized method by which these tests are made. Most concerns interested in contact treating have worked out schemes which fit into their practice and give them the results they want.

On many grades of lubricating distillates the following method is often used. The tests are run in copper beakers of two-liter capacity. Copper is advisable as it not only heats quickly but also cools quickly. Containers made from light sheet steel are also satisfactory. Glass is too likely to crack.

A mechanical stirrer is used. Care should be taken that this does not run too fast; 900 r.p.m. is about right. The beaker is provided with a loose metal cover with openings for the stirrer, a thermometer and one through which a steam jet is introduced. Steam is generated in a boiling flask at one side and is brought into the beaker through a glass tube extending down an inch or so from the top. Both the beaker and flask are heated by gas burners.

A 200-grain sample of oil is taken and the desired percentage by weight of clay is added. The mixture is then heated as quickly as possible to 250° F. and the steam is turned in. The heating is then carried on up to the final temperature. The final temperature often used is set at 50° F. below the flash of the oil being treated. This final temperature is a variable, however, and it is possible that the operator may have to go to the flash temperature or above to get good plant comparisons. When the maximum temperature is reached the heat is taken off and the batch allowed to cool to 300°F. when the steam is taken out and the oil filtered.

With oils other than heavy residual stocks runs are made using 3, 5, 7, 10, 15 and 20 percent by weight of clay. With cylinder stocks or heavy residual stocks the runs are begun at 30 percent and worked backward in five percent drops until a color is reached which is too dark for any practical purpose. These results are plotted in a color/percent by weight curve as described.

In come cases moisture tests are run and the water present taken into account when the curves are plotted, but this would seem to give incorrect figures. The water is often a part of the clay. At least it is present when the clay is used and weighed into the plant process. For that reason if no other the clay should be tested as it is to be used.

The above is a general method which in experienced hands gives good enough results for comparative purposes, but it will generally be found necessary to modify it to suit a particular job. The temperature limit for this apparatus may be taken as 600° F. Many contact-treating plants operate at temperatures running from 700° to 750° F. While there is no difficulty in working at these temperatures in a closed system, doing so in the open, in a batch machine, is not so easy. There is always the possibility of a flash, clay is a very active cracking agent and unless the heating is carried out quickly, considerable of the oil is likely to be cracked and distilled off. There is also an increased chance for oxidation. At best there is some question as to whether or not the results are really comparable to those of the plan. Where it is necessary to work at these temperatures in the laboratory the apparatus should be designed so that it is reasonably tight and provision should be made for a large volume of steam above the heating oil. Some provision also must be made to cool the batch quickly. In a continuous heater the heating and cooling take place over a period of a few minutes, under conditions which promote neither oxidation nor cracking. This should be kept in mind in trying to duplicate such processes on a small scale. If the tests are to be run just for the purpose of testing the clay it will be found that color curves run at lower temperatures will practically parallel those run at very high temperatures. For residual stocks these tests may be run at 450° F. to 600° F.

In general laboratory practice the large Buchner funnels make the most satisfactory filters. Smaller samples such as are used in working up the color/percent by weight curve may be filtered by gravity in small glass funnels.

Oil in the filter cake may be determined by extraction with petroleum ether. For total oil and coloring matter benzol-alcohol should be used. Plenty of time must be allowed for this latter extraction.

In considering decolorization by percolation methods the start is usually made with the filtration itself. The oil in that case is either a raw stock or it has been treated and neutralized. All that is necessary is to put it on the clay and carry it to the required color.

The contact treatment of a sour oil is often thought of in the same way, that is a treatment with fine clay is substituted for a percolation treatment with coarse clay. This is a mistake. If real economy and the greatest benefit is to come from the treat the consideration must go all the way back to the acid treat, and in making a comparison between the two methods those comparisons should in both cases include the costs and yields of the acid as well as the clay treats.

There are special cases, of course, where the fine clay must be used on the neutralized oil, but more often than not it will be found that if the oil be properly acid-treated the clay can be applied direct to the sour oil and a finished product of improved quality will result. Note the term "properly treated." Too often, even when the clay is used direct on the sour oil, the same acid treat is used as if the oil were to be neutralized with soda. This is another mistake. It will be found that when the clay is used on the sour oil less acid is required to produce results equal to those of a soda neutralization, at least so far as color is concerned. To work out the fullest economy it is necessary that there be a balance between the acid-treat and the clay-treat. In this way it is possible to cut down the acid used and the acid-treating loss.

Where the clay is used on a neutralized oil it generally will be found necessary to increase the amount for a

given color over that which would be used on a sour oil.

In working out the contact treat the regular cut-and-try method must be used, working on a range of small acid-treats. Care should be taken that the oil is as free as possible from sludge, though excessive sludge does not cause the trouble with a contact-treat that it does when the oil is to be neutralized with soda. With naphthene- or asphalt-base oils it is possible to use considerably more water for water-settling than is the case when the oil is to be soda-neutralized. It may even be advisable to add several percent of water to the sour oil and agitate it thoroughly before the clay is applied. When the oil carries considerable pepper it will pay to add additional water. This seems to bring down the sludge as a coke with the clay but without clogging its pores.

Paraffin-base oils should almost never be water-settled. If water be used at all it should be kept at a minimum and on no account should an oil of this class be wet when clay is applied. This is particularly true with residual oils and cylinder stocks.

When a sour oil is to be soda-neutralized it should be air-blown before the soda is added, but for an oil that is to be contact-treated this should not be done. Any acid gases that would be blown out by the air will pass off on heating and the excess acidity seems to help the action of the clay.

In finishing heavy residual oils which have been acid-treated there is always difficulty in neutralizing them with alkali. When this is to be done the treating and neutralizing must be done in a solution of water-white distillate, or the crude itself is reduced about 50 percent and this reduced crude or long residuum is treated and neutralized. The neutralized oil is then further reduced. In any event the process is complicated. Where fine clay is used to reduce the acid, the stock may be reduced to any desired specification and acid treated at a high temperature. The sludge may be settled out by gravity or more modern methods use centrifuges. In the contact plant just enough clay is used to remove the acid. The neutralized oil is then taken to color by the regular percolation methods. This scheme does away with the complications and troubles of alkali neutralization. At the same time it takes advantage of the economies of percolation filtration. The loss and expense of the clay treatment are less than that of alkali neutralization while the coarse percolation clay can be reburned and used again. The quality of the finished oil is also much improved.

PERCOLATION FILTRATION

The oldest and best known method in the petroleum industry for the decolorization of oils by means of clays is the percolation method. Plant practice on this line is well established. While each concern may have its own ideas on the subject, they all seem to run pretty much along the same line. Laboratory practice on the other hand is not so well worked out.

Here again many attempts are made to duplicate the scale of the large filters. This is a waste of time as it takes more than scale alone to duplicate the conditions existing in a large filter bed.

For laboratory decolorizations, the finishing of samples, etc., a galvanized iron tube about four inches in diameter and four feet high is useful. This has a conical bottom fitted with a small brass stopcock. Any desired height or weight of clay may be used and any cycle of operation. The latter should be determined by the practice of the plant. Some concerns charge a filter and start taking off cuts as soon as the oil comes through. Others close the filter, charge it full of oil and allow it to stand a specified time before the run is started. Filter rates vary. In any event they should be kept low enough that there will be no channeling. A study of the plant filtration scheme will undoubtedly show some points which may be duplicated on the smaller filters. Whatever is done the procedure should not be too variable and haphazard. After some study and experimental work it should be possible to devise a scheme which will give a reasonably close relation to plant results and plant qualities. This is about as much as can be done and it will be found to be sufficient for all practical purposes. For control work, clay comparisons, etc., the best methods so far developed are those described by S. R. Funsten and H. L. King, Jr. (*Technical Control of Percolation Filtration,* REFINER, Vol. 14, No. 3, March, 1935, and Vol. 14, No. 4, April, 1935). These methods have grown out of a large amount of practical clay work and actual refinery experience. They have been proven in handling the work of a large clay company.

This may seem a meager treatment of an important

PLATE A.

YIELD COMPARISONS

Contact Treatment vs. Acid Treatment in Solution and percolation of Heavy Coastal Red Oil. (Stock A.)

PERCOLATION TREATMENT

Stock A 100%

Acid Treatment.

Solution:
86.77% Stock A.
13.23% W. W. Dist.

Acid Treatment:
26 #/ Bbl. 98% acid.
Treat. loss: 18.27% (on solution)

Yields:
Tr. Solution: 81.73% on solution.
78.94% on Stock A.

From Sludge:
Acid Oil 12.05 gals. } per 100
Slop Oil 1.83 gals. } gals. Sol.

Reduction of Solution

Tr. Red. Stock A...	59.95%
Lub. Dist.....	23.86%
Off Color Dist.....	16.19%
Yield on Stock A...	56.48%

Percolation Filtration:
Loss: 2.0% on Tr. Rd. St. A.
Yields 98% on Tr. Rd. St. A.
55.35% on Stock A.

CONTACT TREATMENT

Reduction:
18.5% Lub. Dist.
Loss: 1.1%

Reduced Stock A
80.4%.....

Acid Treatment:
25 #/ Bbl. 66° acid.
Tr. Loss: 10.0% on St. A Rd.

From Sludge:
Acid Oil 6.6 gals. } per 100
Slop Oil 1.1 gals. } gals St. A. Red.

Tr. Red. Stock A.
Yield: 90%
72.36 on Stock A

Clay Treatment:
10% by wt. Fullers Earth
Loss to clay: 1.1%
Yield: Finished oil 98.9%
71.56% on Stock A

SUMMARIES

	Percolation, Percent	Contact Treatment, Percent
Finished Coastal Lub. Stock	55.35	71.56
Lub. Dist.	22.56	18.50
Acid Oil	13.90	5.28
Slop Oil	2.10	.8
Acid Treatment Loss	5.06	1.96
Clay and Dist. Loss	1.03	1.9
	100.00	100.00

PLATE B.

Cost of Finishing Stock A.—Percolation Method.

Acid Treatment:		
86.77 Gal. Stock A @ .0661 per gal		$ 5.73
13.23 Gal. W. W. Dist. @ .0651 per gal		.86
100.00 Gal. Solution		$ 6.59
Treating cost @ .01 on Stock A		.87
Total cost of treated solution		$ 7.46
Credits: Acid Oil..... 12.05 gals.		
Slop Oil..... 1.83 gals.		
13.88 gals. @ .03		.42
		$ 7.04
Yield: 81.73 gals. treated solution.		
Cost per gallon		.086
Reduction:		
100 gals. treated solution @ .086 per gal		$ 8.60
Reducing cost @ .0045 per gal		.45
Cost of reducing 100 gals. treated solution		$ 9.05
Credits: 16.19 gals. Off Color Dist @ .0651	$1.05	
23.86 gals. Lub. Dist. @ .0643	1.53	
	$2.58	$ 2.58
Cost of 59.95 gals. treated, reduced Stock A		$ 6.47
Cost per gal		.1079
Percolation with Clay		
100 gals. treated reduced Stock A @ .1079 per gal		$10.79
Filtering cost @ .0287 per gal		2.87
Cost of 98 gals. Finished Stock A		$13.66
Cost per gal		.1394

item in oil refining, but as a matter of fact there are few other suggestions that may be given that will have real value. Study the plant processes and the plant results and adapt the filtration scheme to them. That is the only method which will give the latter any real worth.

DEWAXING

Laboratory dewaxing has not been too successful. Various tests have been devised to determine whether or not a given wax distillate will press and here again the experience of the person using them means everything.

In most experimental work it will make little difference whether the stock is dewaxed or not. Usually only in cases where the sample of finished oil is to be put through some sort of an oxidation test must this be gone into and then it is seldom necessary to make a real cold test oil. The stock to be dewaxed—it may be either a distillate or a residual stock—may be greatly diluted with light naphtha, then chilled and filtered in a cold room through a chilled Buchner funnel. Cost and yield figures on dewaxing are usually sufficiently correct if they are taken from the plant figures for the operation.

PLATE C.

Cost of Finishing Stock A.—Contact Treating Method.

Reduction:	
100 gals. Stock A @ .0661 per gal	$ 6.61
Reducing cost @ .0045 per gal	.45
Total cost of reducing Stock A	$ 7.05
Credits: 18.5 gals. Lub. Dist. @ .0643 per gal	1.19
Cost of 80.4 gals. of Stock A Reduced	$ 5.87
Cost per gallon	.0730
Acid Treatment:	
100 gals. Stock A Reduced @ .0730 per gal	$ 7.30
Acid treating cost @ .01 per gal	1.00
Total cost of treating Stock A Reduced	$ 8.30
Credits: Acid Oil..... 6.6 gals.	
Slop Oil..... 1.0 gals.	
7.6 gals. @ .03 per gal	.23
Cost of 90 gals. of treated reduced Stock A	$ 8.07
Cost per gallon	.0897
Clay Treatment:	
100 gals of treated reduced Stock A @ .0897 per gal	$ 8.97
Labor cost	1.00
Clay cost	1.08
Fuel cost	.09
Cost 98.9 gals. Finished Stock A	$11.14
Cost per gallon	.1126

The last question in a process development is: when the work is done and the results are in, how shall they be presented?

Plant methods of showing costs and yields are pretty much the same the world over. After all it is just a matter of accounting. When it comes to showing experimental results, however, and of estimating costs, it is astonishing how many gymnastics the great minds can perform. And one often marvels at the complications they can throw into a really simple matter. In showing yields there can be no better way than the graphic methods which the cost and yields department uses to show plant operation.

In figuring costs each stage should be considered by itself. This makes it possible to pick off a cost at any point. It also irons out complications and makes it possible to follow easily an involved line of work.

Take as an example the results of the treatment and finishing of a heavy Coastal distillate. One method will be by acid treatment in water-white solution, and percolation through coarse clay. The other will be the direct acid treatment of the heavy stock and finishing by a contact treatment with fine clay. This example is valuable here because of the variety of operations shown. It involves the use of a solvent, two methods of acid treating, two types of reduction, and two different methods of clay treating. Either proposition would be hard to show clearly unless it were split up into its separate stages.

Plate A shows a presentation of the yields. In each stage the figures are shown based both on the charge for that particular operation and also figured back on the crude stock, in this case on Stock A. At the end these last are tabulated in the summary.

This comparison is an excellent example of how the various plant operations depend on each other and why, in judging a process or a procedure the development men should go far enough back that he may be certain that he has the whole story of the changes that this hoped-for improvement will make.

Here essentially, it is proposed to substitute a treatment with fine clay for a treatment with coarse clay. By using a contact treat we can do away with the acid treatment in solution and the neutralization with alkali.

Stock A, the base stock, has been cut in a shell still with the idea that the treated and neutralized solution will be further reduced to specification. For this reason it is cut lighter than would be the case if it were to be handled without dilution. Before this stock can be contact treated it must be reduced. It will be seen that while practically the same quantity of acid is used in either case with the solution treat 98 percent acid is used while in the contact treat 66° Be. is employed. The first real comparison between the two comes at the end of the reduction in the former and at the end of the acid treat in the latter. Here we have a yield of stock to be decolorized of 56.48 percent on Stock A as against 71.36 percent on Stock A for the contact treat.

In the decolorization stage there is a slight advantage in favor of the contact treat as far as yield is concerned, but it is clear that the real gain in yield comes in the acid treat.

Plate B and Plate C show the costs of the two methods based on the yields shown in Plate A.

(Continued on page 119)

Combustion *Phenomena In the* Natural Gas Engine

PART II

JOSEPH LISTON
School of Mechanical Engineering
University of Oklahoma

IN a recent article methods of calculating air-fuel ratios for natural gases and effects on performance of varying the air-fuel ratio were discussed. (Refiner, Vol. 15, No. 2, February, 1936, page 73). Briefly, the following conditions were observed:

1. Although the heating value of the different hydrocarbons composing natural gas varies widely, the heat energy per cubic foot of chemically correct air-fuel mixture is nearly the same for all of the gases.

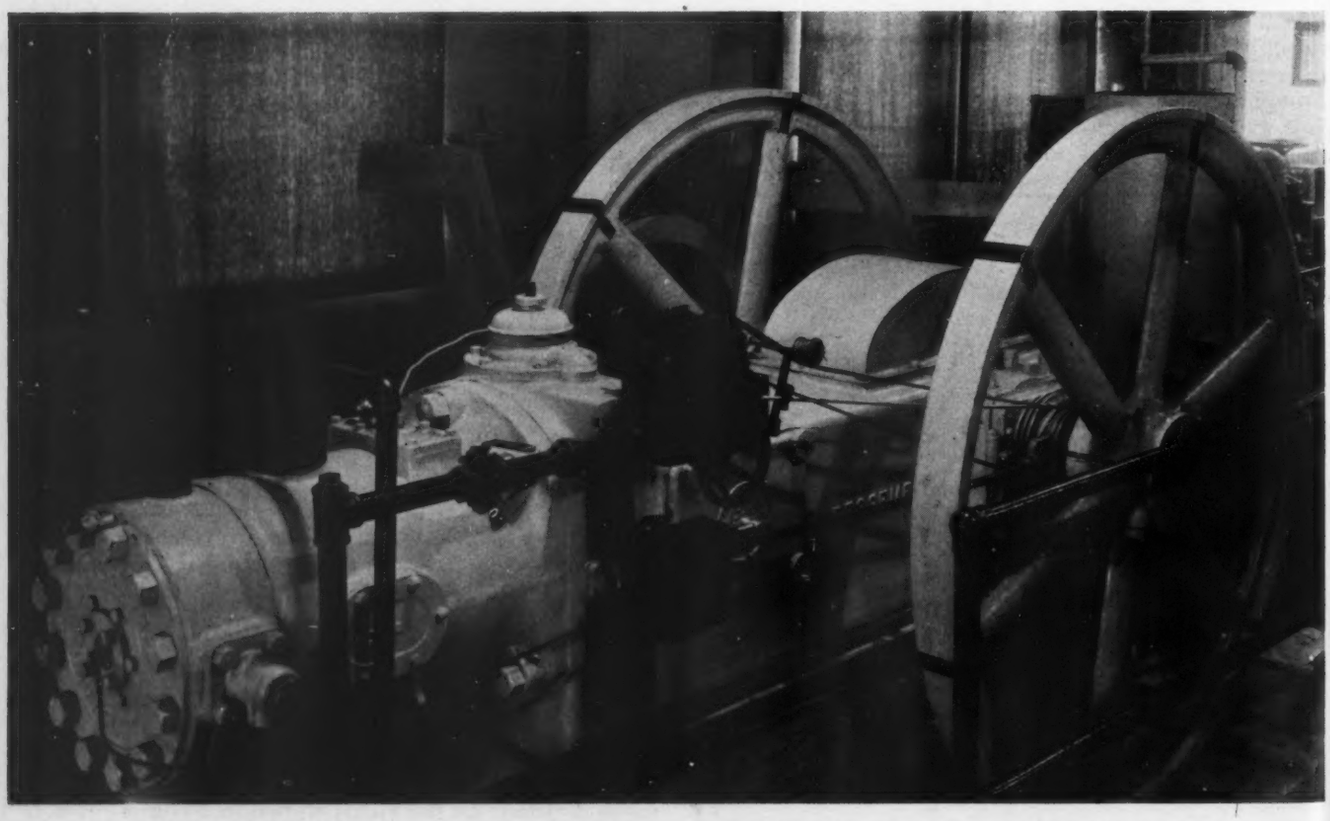
2. The power that an engine can theoretically develop is determined by the heat energy per cubic foot of air-fuel mixture rather than by the heat energy per cubic foot of fuel, hence, the power that a gas engine can develop will not vary greatly with natural gases of different composition providing proper adjustment for air-fuel ratio is made.

3. Theoretically either an excess of air or fuel will decrease the power output and efficiency.

Seemingly, very little effort has been expended in attempts to correlate theoretical and actual combustion phenomena in gas engines. Considerable work has been done in determining the effects of air-fuel ratio in gasoline engines, and the assumption that parallel results would be had in gas engines is reasonable, but this does not tell us what air-fuel ratios are best or what the effect of minor air valve adjustment will be.

To investigate this situation, tests on the 35 horsepower, 2-stroke cycle, natural-gas engine shown in Figure 5 were recently conducted in the Mechanical Engineering Laboratories of the University of Oklahoma. The engine is of conventional design, and, although smaller, it is very similar to many petroleum industry installations, a fact which should make the test results of direct use to many operators.

The power output was measured with a Prony brake. Fuel consumption was measured with a gas meter, and air consumption for the tests, was found from indicator cards on the scavenging or compressor end of the cylinder. The fuel enters the compressor cylinder and mixes with the air before entering the



Tests reported were made on this 35-horsepower, 2-stroke cycle natural gas engine.

power cylinder. The method used in calculating the air-fuel ratio is as follows:

The volumetric efficiency of the compressor cylinder is the ratio of the volume of new charge to the suction displacement volume. The volumes may be based on one cycle or any convenient unit of time. The air may be measured in either of two ways. A large meter may be attached to the air intake (a surge tank is usually necessary between the meter and the engine to take care of the intermittent flow into the cylinder) or the volumetric efficiency may be found from indicator cards on the scavenging cylinder.

Metering the air is possibly the more accurate method, but it has the disadvantage of greater complexity, and the obstruction to the flow of air through the meter, piping, and surge tank will tend to change the volumetric efficiency so that test conditions will not be truly representative of ordinary operating conditions.

Possible errors in the indicator method are those typical of all indicators, that is, indicator inertia, inaccurate phasing, excessive pencil friction, etc. However, with sufficient care these sources of error can be minimized.

Referring to Figure 6, the volumetric efficiency for run number 4 as measured from this card is 55.02 percent.[1] The scavenging cylinder on this engine has a diameter of 12 inches and a stroke of 16 inches.

[1]The volumetric efficiency on this engine is considerably lower than it should be. Because of low fuel pressure, it is necessary to restrict the air to get the proper air-fuel ratio. This is no fault of the engine design.

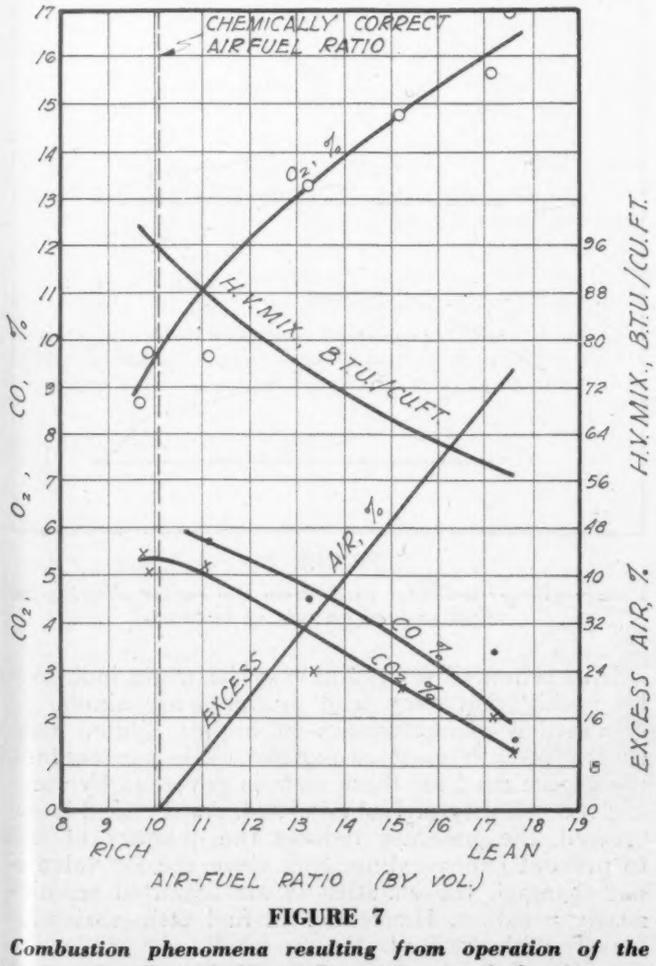


FIGURE 7

Combustion phenomena resulting from operation of the engine shown in Figure 5 at various air-fuel ratios.

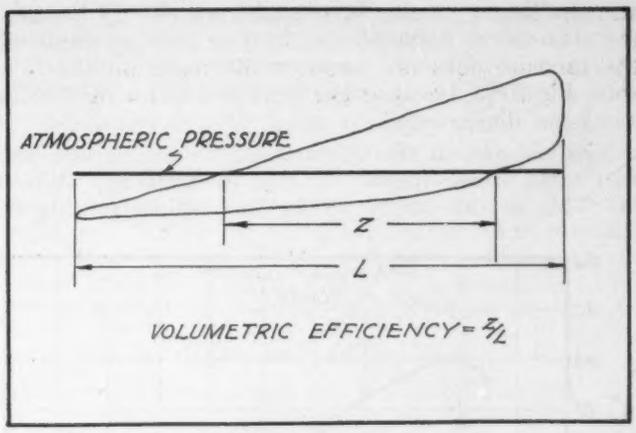


FIGURE 6

Two stroke cycle gas engine scavenging card illustrating the method of determining air-fuel ratios. The volumetric efficiency of this card is low due to low fuel pressure which necessitates pinching the air flow.

The diameter of the piston rod is 2.25 inches. The engine speed was 232 R.P.M.

The suction displacement per minute is:

$$\frac{(12^2 - 2.25^2)\frac{\pi}{4} \times 16}{1728} \times 232 = 234 \text{ cu. ft.}$$

The volume of charge per minute is:

234 x .5502 = 129 cu. ft. at the observed atmospheric conditions of 28.74 inches Hg. and 79.5°F. Hence the volume at standard conditions is:

$$V_o = \frac{520 \times 28.74 \times 129}{29.92\ (79.5 + 460)} = 119.7 \text{ cu. ft.}$$

The observed volume of fuel for run number 4 measured at 85.8°F. and a pressure above atmospheric of 9 inches of water was 9.3 cubic feet per minute. Hence, the volume at standard condition is:

$$V_o = \frac{520\ (28.74 - 9 \times .0735) \times 9.3}{29.92\ (85.8 + 460)} = 8.7 \text{ cu. ft.}$$

The volume of air is 119.7 — 8.7 = 111 cu. ft., and the air-fuel ratio for this run is:

$$A/F = \frac{111}{8.7} = 12.76 \text{ (by volume)}$$

By varying the position of the bell on top of the cylinder, Figure 5, a greater or less restriction of the passage way into the scavenging cylinder can be attained. By this means the volumetric efficiency can be varied over the entire range of air-fuel ratios at which the engine will operate. A multiplying lever-indicator, not shown in Figure 5, was connected to the bell so that very close adjustment of the air supply could be made.

During the tests sufficient data were taken to determine the information given in Figures 7 and 8. The fuel analysis was as follows:

Constituent Gas	Percent by Volume (60 °F. and 14.7 lbs. per sq. in. abs.)
CH_4	92.5
C_2H_6	7.1
CO_2	0.4

Referring first to Figure 7 and comparing it with Figure 4, it is seen that the percentage of excess air

and the heating value of the mixture closely parallel the theoretical values for CH_4. The heating value of the mixture does not begin to decrease on the rich side, Figure 7, because the heat to carbon monoxide has been disregarded.

The oxygen in the exhaust is, for any given air-fuel ratio, much higher than it theoretically should be. This is due partly to the incomplete mixing of

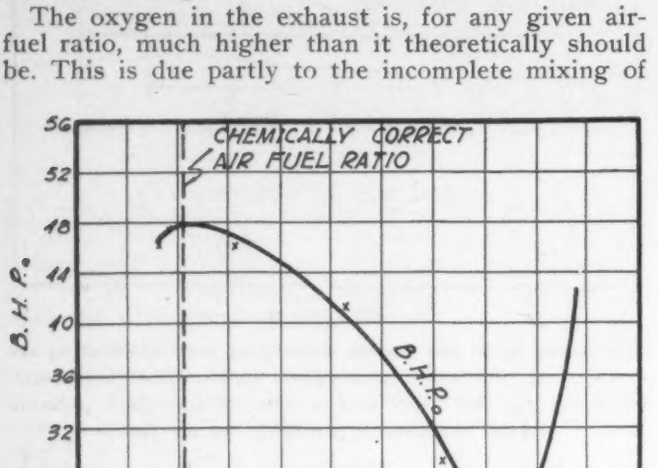


FIGURE 8

Effect on performance of operating the engine shown in Figure 5 at various air-fuel ratios.

the fuel and air with resulting incomplete combustion of some of the carbon. When new charge is entering, the exhaust port is open and some new charge escapes directly to the exhaust. Once in the exhaust pipe, the oxygen and fuel will not combine because they are below combustion temperature.

The prevention of the escape of new charge directly to the exhaust is a serious problem in two-stroke cycle gas engines. By admitting fuel to the power cylinder directly after the ports are covered by the piston, waste of fuel to the exhaust is eliminated, but the time for mixing the charge is lessened. This would probably necessitate additional excess air to permit reasonably complete combustion, and that might, in turn, slightly reduce the power output. Unfortunately, very little comparative data are available.

Exhaust Waste

Waste to the exhaust may be eliminated largely by proper design of the exhaust-pipe system. With the correct length of exhaust pipe, pressure surging in the pipe will be timed to prevent loss of new charge to the exhaust and yet give satisfactory scavenging of the burned gases. Tests now in progress show that very decided changes in performance result from changing the exhaust-pipe length.

While at first thought exhaust-pipe length may appear to have relatively little bearing on combustion phenomena, in reality it is quite important in that it so largely determines how completely the cylinder is scavenged of burned gases. Residual or burned gases in the cylinder act to reduce engine performance in two ways. (1) When more burned charge remains in the cylinder, less new charge can enter, and (2) with increased dilution of the new charge by the burned charge, combustion characteristics are changed. The mixing of excessive quantities of inert, (i.e., already burned) gas tends to separate the fuel and oxygen molecules farther apart so that the rate of burning is retarded. This reduces the power output and efficiency.

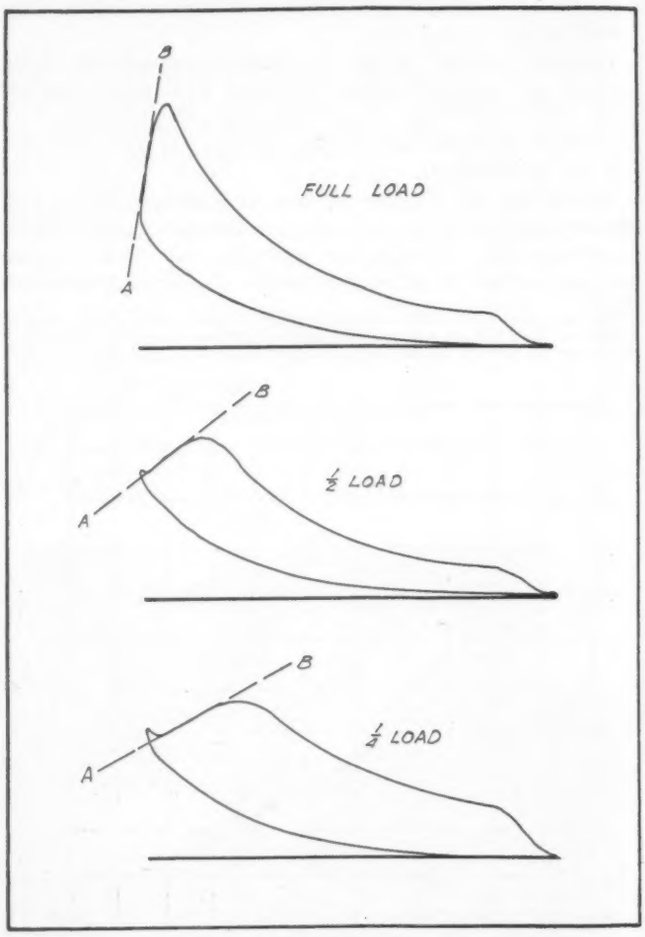


FIGURE 9

Power cylinder indicator cards from the engine showing the effect of load on rate of burning.

Illustration of this point may be made indirectly by noting that very lean mixtures are similar in combustion characteristics to highly diluted mixtures. As with most two-stroke cycle gas engines, the engine used for these tests is governed by varying the quantity of fuel admitted. As the load is decreased, the governor reduces the quantity of fuel to prevent overspeeding, and, since the air valve is not changed, the quantity of air admitted remains nearly constant. Hence the air-fuel ratio varies inversely with the load.

In Figure 9, the cards at light load also represent

lean mixtures. The slope of the pressure rise line A-B during combustion is a measure of the rate of burning, and, as the slope becomes less and less steep with decreasing load, the logical conclusion is that the rate of burning is less rapid for lean mixtures.

Figure 10 shows that the fuel rate in cubic feet of gas per BHP hour increases with decreasing load. The relation between fuel rates and thermal efficiency is

$$BTE_o = \frac{2545}{BSFC_o \times H.V.}$$

Where BTE_o is the brake thermal efficiency, i.e., the part of the heat supplied that does useful work, based on standard conditions.

$BSFC_o$ is the brake specific fuel consumption in cu. ft. per brake horsepower hour corrected to standard conditions.

H.V. is the number of B.t.u. per standard cu. ft, for the fuel.

From this equation it is seen that, for any given fuel, the efficiency varies inversely with the specific fuel consumption, and in view of its effect on this latter quantity, air-fuel ratio is a major factor in gas engine efficiency.

The question naturally arising from this is why not govern the mixture of air and fuel rather than just the fuel alone and thereby keep the air-fuel ratio constant with changing load? This method can be used in 4-stroke cycle engines, but, if this is done with the 2-stroke cycle engine, the volume of new charge becomes too small at light loads to effect good scavenging. Then excessive dilution-results, and conditions are as bad if not worse than with lean mixtures. Numerous auxiliary devices have been suggested to get around this difficulty, but they either add excessively to the complexity and cost or do not function properly. Hence, for the present at least, the 2-stroke cycle gas engine remains primarily suited to constant or near constant load operation and that load should be near rated for best operation.

During the above series of tests, the sensitivity of the engine to air-valve adjustment was particularly noticeable. Very slight changes in position of the bell made rather marked changes in the air-fuel ratio, the power that the engine could develop, and the economy of operation. In fact, the tests could only be completed after a multiplying lever-indicator was installed. This device served to magnify the motion of the bell and thereby enabled closer adjustment.

The significance of brake specific fuel consumption may possibly be made clearer by means of an example. Suppose, for this purpose, that by more accurate adjustment, an operator succeeds in decreasing the B.S.F.C. of his 5-100 horsepower engines from 15 to 11 cubic feet of fuel per brake horsepower hour. In a 300-day year of operation at, say, 12 hours per day, the fuel saving would be

(15 to 11) 100 x 5 x 12 x 300=7,200,000 cu. ft.

At 5 cents per thousand this would be a saving of

$$\frac{7{,}200{,}000}{1{,}000} \times .05 = \$360.00$$

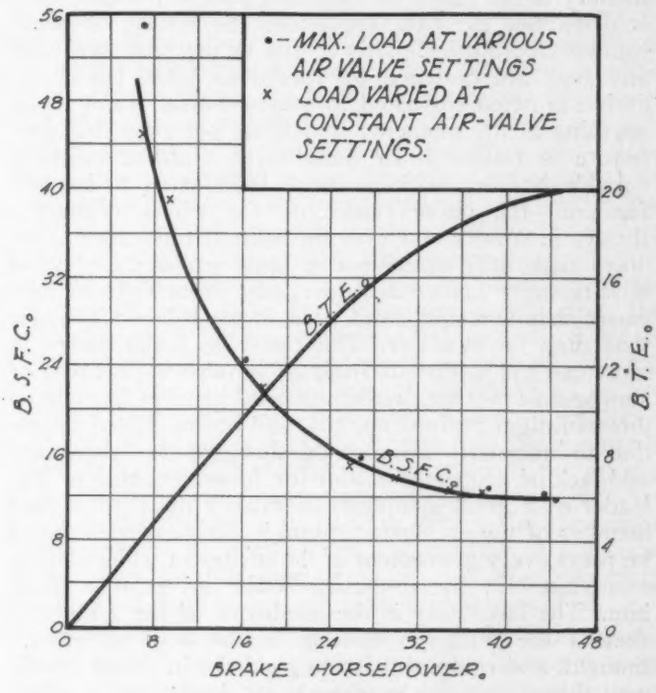
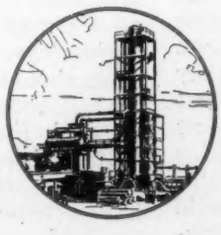


FIGURE 10

Variation of specific fuel consumption and efficiency with brake horsepower for the engine shown in Figure 5.



DESIGN OF
Routine and Semi-Routine Refinery Laboratories

HARRY VINOCK

IN this article concerning laboratory design, the author lectures, and does so critically, and offers some excellent suggestions. Many chemists will agree with his views and feel that he is due praise for terming the spade the spade that it is. Some, in new and modern laboratories can look back upon times when those laboratories were not new and modern and rejoice. Others, not chemists, but executives, can do well to give his arguments thought—for time and human energy and efficiency are money. Not all laboratories are badly designed, that is true. Most of them simply are not designed. Many others beggar description and these are too many.

MANY oil refinery laboratories, like Topsy, just grew. While practically all other equipment in the refinery is the result of deep and patient thought, such is often not the case for either the testing or semi-routine laboratories. This is due to the fact that stills and such are designed by specialists while laboratory design is often entrusted to someone who is not doing anything at the moment; sometimes not even that procedure is followed. In some cases someone builds a sizeable building without much thought as to its true function—the nerve center of the whole refinery—throws in sundry and (for the sake of misguided economy) makeshift equipment in some semblance of what is laughingly known as order, and from time to time tosses in other equipment as it is needed in any space that may be available. The resulting hodge-podge in most cases is inefficient from all standpoints because of slowness of testing, worker fatigue, worker inaccuracy due to fatigue; mixed-up, lost, and contaminated sample due to unorderly progression through the laboratory, and lack of proper provision for future expansion. The leader of a great symphony is usually the highest paid member of the orchestra; through direction and control he plays every instrument in the orchestra while playing none himself; the orchestra could not exist without him. The laboratory is the conductor of the symphony that is the refinery; nothing in the way of money, thought, and equipment is too good for it. More intelligent thought should be given to its design and working smoothness, the disposition of its equipment, provision for its integrated future expansion, and the welfare of its most important units, the workers. It is the purpose here to review the most important factors in the design of straight routine or testing laboratories for such tests as flash, fire, cloud, pour, and distillation; and semi-routine laboratories where various special and chemical tests are run.

LIGHT

Poor lighting is one of the greatest contributing factors to testing mistakes that we have to contend with as it is a major cause of worker fatigue. For adequate daytime lighting the windows should be of a maximum possible area. They should not be of the sash variety but rather of the steel frame type which open like doors and which give the greatest glazed area per window area. They should extend from as close to the floor as practical to almost the ceiling. So that the greatest lighting and ventilation benefits should accrue, there should be no shelves or other hindrances in front of the windows. Skylights if possible should also be provided. For night and dull days artificial lighting of the direct-indirect type is necessary. Raw bulbs should never be used. To eliminate glare and shadows the walls and ceilings should be painted with a white paint of good light reflecting qualities. The lowest light intensity at any point should always be that prescribed for reading of fine print by the Illuminating Engineers Society and as shown by the Weston sight meter. It must be remembered that a worker with eye strain is always either a slow or unreliable worker. Specially designed lights should be used for special purposes.

VENTILATION

In all laboratories there are always present fumes which if allowed to remain become fire and health hazards. Ample provision should therefore be made for general ventilation through large windows and through forced draft ventilation fans near the ceiling which not only remove noxious fumes but also remove the superheated layer near the ceiling which tends to depress worker efficiency during the summer months. In the chemical sections adequate closed hood provisions should be made.

FLOORS

The subject of floors may at first seem out of place in a discussion of laboratory design; however, since practically all laboratory work is done while standing and since there is nothing that will so effectively distract a man's attention from his work as sore feet and aching legs, the subject assumes importance. Floor surfaces should never be made of hard unyielding surfaces such as concrete, nor should foot breaking duck-boards be used. Floor surfaces should be covered with some plastic chemical and oil-proof preparation of which there are several on the market. These preparations have a certain amount of give to them and are very easy on the feet. Wood flooring is obviously out.

SAFETY

Even in the best regulated of laboratories fires and accidents happen. Adequate fire fighting apparatus should be used. For the protection of workers whose

clothes may catch fire there should be provided showers at convenient points under which the men can stand. A few blankets for the purpose of smothering burning clothes are also essential. A very good arrangement is to place the showers in alcoves the floors of which upon the application of weight operate the shower valves; a blanket is then hung from a U-shaped rod by fasteners which easily come loose on the application of tension. When a man whose clothes are burning enters the alcove, the shower starts immediately, and if the fire needs smothering, all he needs to do to wrap the blanket around himself is to grab the edges and pull. In order that the extinguishing of fires shall not entail other than fire loss it is recommended that carbon dioxide fire extinguishers be used. For emergencies in which fire inside the laboratory may get out of control a system of jets connected to a steam line and controlled by valves outside of and some distance from the laboratory is suggested. If possible, this arrangement should be connected to a carbon dioxide reservoir rather than a steam line since anyone so unfortunate as to be trapped in the building can die from steam inflicted burns as easily as from fire burns. Ample fire escapes and exits should be provided. This last may seem too elementary to mention, but there is one laboratory from which the only exit from the upstairs portion is by an outside stairway. If the door to this stairway should be blocked by a sudden conflagration, as sometimes happens, the only recourse the men could then have for escape would be to jump from the windows, and the windows are blocked by tables lining the walls. First aid kits should always be provided, and the men should be trained in their use. Laboratory injuries are many times of such special and extraordinary nature that immediate first aid is imperative.

DISPOSITION OF EQUIPMENT

Unplanned disposition of equipment probably uses up more valuable time in oil laboratories than any other one single cause. While there are kitchens in which the location of each and every article has been carefully thought out so that the housewife will have to make the minimum of steps during the preparation of a meal, many laboratories are evidently planned by an entirely opposite motivating idea, that is, the location of every article has been carefully thought out so that the testers will have to make the maximum number of steps for the completion of any test or series of tests. A good illustration of the case in point is afforded in one of the larger refineries. In this refinery one man is assigned to the testing of paraffin samples which entails that he determine the percent naphtha by steam distillation, and the determination of the melting point and tensile strength on the residue after the distillation; these last two tests are run in a special constant temperature room or cold room. The overall dimensions of the laboratory are about 50 by 40 feet. Let us follow the operator while he runs these three tests. First the samples are brought in by a sample carrier and placed on a sample table in the front center of the laboratory. If the sample has solidified, which is usually the case, the operator has to take it to the hot box, 20 feet away; he then pours the sample into a flask and distills it on a special permanently installed steam distillation rack which is about 25 feet from the hot hox; the distillation being completed the residue is then carried practically the whole diagonal length of the laboratory or about 45 feet to the corner where the cold room is situated so that he may run the melting point and the tensile strength tests. Since there are considerable time intervals in the different tests and since the tester is usually running from three to four samples at a time, he is continually running from the cold room to the distillation rack to the hot box to the distillation rack to the cold room and back again; needless to say, the resulting waste of nervous and physical energy and time is enormous. The illogical truth of the matter however is that just outside of the cold room door is a work desk used for general purposes which could be easily fitted with a small hot box underneath while the table part could easily be used for a combination sample table and distillation rack. If this were done, the tester would be saved on the average from three to four miles of walking and from an hour to two hours of time per day. In the same laboratory the grease tester also lives a nomadic existence due to a studied spacing of his equipment throughout the laboratory. A little observation should bring to light many like cases in practically any oil man's experience. In the ordinary testing laboratory a lesson may be had from the automobile industry in its assembly line and conveyor systems. The progression of tests should be so arranged that the least possible time should elapse for a whole series of tests; this would require a detailed study of the various tests as to the amount of sample needed, time required for the test, general procedure for the test, final disposal of the sample, and the number of men available during the day and during the night. In general those tests using the least amount of sample and taking the most time should be run first. For instance take the simple series of gravity and flash. If the gravity is run first, the flash operator has to wait until the gravity tester is through with the sample and there is a risk of contamination of the sample that may throw the flash off; if however the sample goes first to the flash man, he draws off the small amount of fresh material that he needs and immediately sends the remainder on to the gravity man; time intervals are thus so sandwiched that the gravity and flash are finished in almost the same time that it would otherwise take for just one of the tests. Thus considerable time is saved and the important item of inaccuracy through contamination avoided.

A suitable means of conveying samples through the laboratory should be worked out. This may either by by a system of mechanically operated conveyor belts or by a system of sheet iron troughs on which samples may be slid from one operator to the other like beer mugs along a bar. By this arrangement the problem of determining whether or not all tests have been run on any sample is greatly simplified as no sample which has been finished will remain on the conveyor chain or trough. At the beginning of the chain there will be only fresh samples; the samples at the end of the chain are those ready for disposal or storage. Gadgets should be carefully designed beforehand and installed as permanent equipment. As far as possible these gadgets should be designed to remove the element of human fallibility from the determination of arbitrary standard tests. Examples of such gadgets are motor driven stirrers for Pensky Marten flash apparatus and a special light for use in determination of cloud tests.

The semi-routine laboratory is a much harder problem; however, some general rules are not amiss. Equipment for special tests such as for instance grease tests should be permanently installed in one compact well-designed group and so supplied with facilities that the operator will not have to move more than a few steps during any test. Equipment such as ovens used by the

(Continued on page 119)

Fractionation *of Petroleum Residues and Heavy Crudes by Means of* Natural Gas By PILAT'S METHOD

DR. M. NAPHTALI
Berlin, Germany

IT HAS been known for several decades that the asphaltic constituents of petroleum can be precipitated by means of light hydrocarbons. Holde had practiced this method some 30 years ago at which time a patent had been taken out by him to deasphaltize petroleum residues with gasoline.

In 1922, the Methan Institute of Research, Lemberg, following the work of K. Kling, suggested separating asphaltic material from petroleum, using very light hydrocarbons, which was based on the fact that the lighter the hydrocarbon, the more complete is the precipitation of asphaltic matter.[1]

Polish petroleum was precipitated by gasolines of various boiling points: Gasoline of 82-92° C.B.P. yielded 2.6 percent asphalt, after employing a dilution of 5 parts of gasoline to 1 of crude. Similarly, gasoline of 32-42°C. B.P. yielded 8.7 percent, and a light cut of B.P. 5-8°C. B.P. yielded 13.4 percent of asphaltic matter. The asphalt separated in such manner was free from paraffin, provided the precipitation is carried out at room temperature, or at some elevated pressure. Without the previous removal of gasoline, kerosene and gas oil by topping one could only obtain 1.6 percent of asphalt by thinning the crude forty-fold with the same gasoline.

In 1932 S. v. Pilat and M. Godlewicz repeated the work of Kling with a propane-butane fraction, obtained in the stabilization of natural gas, consisting of 61.2 percent propane, 34.63 percent *iso*-butane, and 4.17 percent normal butane. In treating a crude residue with this fraction, they had observed that the solution above the precipitated asphalt was still dark colored. In spite of this efficacious agent, the coloring matter and asphalt were not yet completely removed from the oil. In order to augment the effect of the propane-butane mixture, and to extend this effect to the soluble dark colored bodies of asphaltic matter, dry natural gas (97 percent methane), a still lighter hydrocarbon, was introduced into the deasphaltized solution in a pressure bottle. At a pressure of about 30 atm. A dark semi-fluid product was precipitated and the color of the supernatant solution changed to a light yellow. Upon injecting still more natural gas into the pressure bottle, a heavy oil precipitated as a second phase, which was liquid. In gradually raising the pressure and therefore the concentration of the gas, still lighter oils were gradually precipitated. When a pressure of 130 atm. had been reached, only a small percentage of light yellow-colored oil remained in solution in the propane-butane mixture saturated with natural gas or methane. By this means a complete fractionation of the petroleum residue at room temperature had been attained.[2]

The process of separation is due to the diminishing solubility of high molecular weight hydrocarbons, when the concentration of methane is increased by means of pressure. The natural gas employed consisted of 97.9 percent CH_4, — 0.72 percent C_2H_6, — 0.18 percent C_3H_8, — 0.12 percent C_4H_{10}, 1 percent nitrogen, and 0.03 percent carbon dioxide. Practically, the pressure gas may be denoted as methane. Investigations of F. Fischer and Zerbe[3], and P. K. Frolich[4] show that the solubility of methane in different hydrocarbons is not only dependent on the increasing molecular weight, but also on the chemical nature of the solvent. For instance, propane is a better solvent for methane than hexane, hexane is better than cyclohexane, and this again better than benzene. For nearly equal molecular weights, the solubility of methane gradually diminishes from paraffins to naphthenes with many side-chains, to the simpler naphthenes, and finally is least soluble in the aromatics. On the other hand it is assumed that the gases precipitated from a solution principally those constituents that are bad solvents for the same gases, and further that in different gases the precipitating power is relative to their solubility. The effect of hydrogen is similar to methane. But as the solubility of hydrogen in propane is much less than that of methane a higher pressure must be applied. For instance, 120 atm. of hydrogen pressure secures only the same quantity of precipitated asphalt or heavy oil as does natural gas under 30 atm. pressure. Nitrogen shows a value midway between the two gases above, and this is in conformity with the statements of Frolich for the solubility of this gas in petroleum products. The following experiment shows the precipitating effect of different gases on the solution of a deasphaltized Venezuela residue in a propane-butane fraction. In order to exactly determine the initial precipitation, a ratio of deasphaltized residue to solvent of 1 to 6.1 was employed. The pressure was determined at which a cloudiness was observed. The following results were obtained:

With CO_2	Nat. gas (97.9% CH_4)	Nitrogen	Hydrogen
15 atm.	18 atm.	28 atm.	Not cloudy at 86 atm.

This sort of fractionation obviously depends on the character of the solvent used. After the asphaltic constituents of a petroleum residue were removed by solution of the residue in propane-butane, followed by filtration, the deasphaltized solution was then freed from the solvent; the oil-mixture remaining was then dissolved in a five-fold quantity of petroleum ether of gravity 0.627, and 33°C. end-point. By pressuring more methane into the flask containing this solution, the precipitation of a second phase will

TABLE 1

Fractionation of a Roumanian petroleum residue

Pressure (Atm.)	Quantity In g.	Yield Percent	Specific Gravity	Viscosity 37.8 °C.	Saybolt 50 °C.	Saybolt 98.9 °C.	Viscosity Ind.	Viscosity Gravity Constant	Pour-Point °C.	Flash-Point °C.
8	805	27.35	.....	....	....	.....	..	.....	.....	....
30	137	4.65	0.997	....	....	2202	..	0.906	.....	....
40	261	8.85	0.9845	....	....	1122	..	0.897	.....	....
50	145	4.95	0.960	26658	8533	422	..	0.869 0.878 0.865	..... + 8	....
60	278	9.45	0.9495	10366	3802	260	58	0.870 0.855	+ 5.5	275 ....
70	273	9.27	0.939	6354	2468	202	61	0.861 0.849	+ 4	277 ....
80	206	7.00	0.9295	3703	1523	151.1	64	0.853 0.845	+ 9	267 ....
90	188	6.40	0.9225	2363	1027	118.5	64	0.847 0.842	+ 3	263 ....
100	128	4.35	0.9165	1602	725	95.2	60	0.844 0.834	0	....
130	154	5.25	0.909	1056	502	78.3	62	0.838 0.844	— 6	249 ....
Rest	122	4.15	0.908	615	315.8	61.4	57	0.842	—13	....

Feed Stock: (Rumanian residue): specific gravity 0.9735, Viscosity E. 100 °C. 17, fl. p. 269, 2945g, pour point +12°C.
One part asphalt-free residue was diluted with 4.65 parts of the following hydrocarbon-mixture: Propane 61.2 percent, Isobutane 34.63 percent, Butane 4.17 percent.

begin at about 130 atm. whereas in propane solution the same effect takes place at 30 atm., because as explained above, propane is a better solvent for the natural gas than the pentanes, which is the main portion of the petroleum ether. Ethyl ether shows a similar effect.

The mole-fraction of methane in the propane-butane mixture at 100 atm. and 20°C. is 0.564, in good conformity with Sage, Lacey and Schaafsma[5] who found this mole fraction to be 0.574 at 95 atm. and 20°C.

The thermal effects accompanying the process of dissolving methane in hydrocarbons, according to the investigations of E. Neyman and Pilat[6] are practically restricted to the heat of compression of natural gas. This is obvious since the solution takes place at temperatures far above the critical point and the heat of solution of related hydrocarbons requires but little heat transformation.

Calorimetric measurements showed that a pressure bottle partly filled with propane takes up at equal pressure more methane than an empty one. For instance, in a calorimetric bomb of 267.6 cu. cm. capacity, the weight increased after filling with methane to 51 atm. at 16°C. approximated 9 gms. If the bomb had previously contained 33.4 gm. propane, then the weight increased at 50.5 atm. of methane to 10.15 gms.; with a propane content to 100.8 gms. the increase was 10.5 gms.; however, in the presence of pentane and heavier hydrocarbons the quantity of methane introduced by pressure decreases with the filling of the bomb. Plotting as ordinates the increase of pressure needed to saturate the propane solution of a petroleum residue with methane, a break will be found in the curve at some point in the time scale; that is, a great increase in pressure will correspond to a relatively small increase in weight. The progressive solution of methane corresponds to an increase of the volume of the fluid which again depends on the concentration of methane; at some certain high pressure the vessel is completely filled, and at this point the concentration of methane cannot be further increased; this is the point at which one notices a break in the above-mentioned curve. If it is intended to work up to a final pressure of 110 atm. the vessel cannot be filled to over half its capacity.

By injecting methane into a solution of an oil-mixture in propane, the oil having been previously freed from asphalts and aromatic coloring matter, Pilat expected to be able to precipitate lighter aromatic constituents as well as high molecular weight oils of paraffinic nature. This suggestion was confirmed by the following experiment: A lubricating

TABLE 2

Fractionation of Venezuela-Residue

Pressure (Atm.)	Quantity In g.	Yield Percent	Specific Gravity	Viscosity Saybolt 37.8 °C.	Viscosity Saybolt 50 °C.	Viscosity Saybolt 98.9 °C.	Viscosity Ind.	Viscosity Gravity Constant	Pour-Point °C.	Flash-Point °C.
8	2125	49.4	.....	....	....	.....	..	.....	.....	....
30	336	7.8	1.004	....	....	3730	..	0.908	.....	....
40	257	5.95	0.9885	....	....	1757	..	0.896	.....	....
50	293	6.8	0.9665	....	....	731	..	0.876	+ 9	293
60	204	4.75	0.9535	....	9601	456.7	..	0.871	— 1.5	284
70	238	5.55	0.9455	18181	6098	334.6	43	0.850 0.862 0.843	..... — 3	.... 283 ....
80	169	3.95	0.9365	10303	3715	245.6	49	0.854 0.842	— 2	288 ....
90	157	3.5	0.9300	6160	2353	186.6	50	0.850 0.837	—14	264 ....
100	123	2.85	0.923	3798	1522	145.9	54	0.845 0.835	—18	264 ....
130	135	3.15	0.9145	2166	925.4	106.6	50	0.839 0.834	—18	264 ....
Rest	85	2.0	0.906	1023	470.2	72.5	41	0.836	—18	264

Feed Stock: (Venezuela residue) 4300g; Specific gravity 1,019, Viscosity E. 100 18, fl. p. 291, pour point +44 °C.
One part asphalt-free residue was diluted with 4.35 of the same hydrocarbon-mixture v. Table 1. †).
†Oel, Kohle, Erdol, Teer II. 637 (1935).

TABLE 3

Fractionation of Harklowa residue (Polish)

Pressure (Atm.)	Yield Percent	Specific Gravity 15.6 °C.	Viscosity, Engler		Viscosity Ind.	Viscosity Gravity Constant	Pour	Flash	Conrad. Carbon	Mol. Weight	Acidity	Sap. No.
			50 °C.	98.8 °C.								
8.....	20.9	1.026	.....	....	..	.....	.....	256	....	...	1.67	....
40.....	15.5	0.9905	.....	19.4	..	0.912	6 C	235	8.4	548	1.1	1.9
50.....	7.4	0.9705	175	8.64	..	0.896–0.875	— 1 C	233	4.7	528	0.98	1.37
70.....	20.9	0.9470	42	3.95	44	0.875–0.877	3 C	228	1.7	464	0.55	0.72
100.....	18.9	0.9275	15.27	2.34	44	0.862	— 8 C	216	0.44	439	0.28	0.58
Residue....	15.0	0.9065	4.26	1.55	51	0.853	—18 C	181	0.06	397	0.08	0.30

Feed Stock:—10,300 grams; Specific gravity 0.964; Viscosity Engler 100 °C. 55.1; Flash point 217 °C.; Pour minus 7°C.; solvent used: propane 89 percent, butane 11 percent.

oil fraction, which showed a specific gravity of 0.9275, viscosity E.50°C. of 15.27 and 2.34 at 98.9°C., with a V.i. of 44, precipitated by methane between 70 and 100 atm. was distilled to 66 percent overhead by vacuum at 0.2 mm., without using a tower. Distillate and the 33 percent residue show:

	Distillate 66 Percent	Residue 33 Percent
Specific Gravity	0.9315	0.9190
Viscosity E. 50°C	9.02	40.7
Viscosity E. 98.9 °C	1.85	4.28
Viscosity Index	19.0	71.0

The specific gravity of the more viscous residue is less than that of the distillate. Another fraction recovered as before, and which showed a specific gravity of 0.928; visc. E. 50°C. 18.98; visc. E. 98.9°C. of 2.59, with a V.i. of 46, equivalent to a viscosity-gravity constant of 0.860, had likewise been distilled to a 33 percent overhead by vacuum, and distillate and residue showed:

	Distillate 33 Percent	Residue 66 Percent
Specific Gravity	0.927	0.931
Viscosity E. 50 °C	5.69	40.15
Viscosity E. 98.9 °C	1.61	4.32
Viscosity Index	44.0	72.0
Viscosity Gravity Constant	0.876	0.855
Molecular Weight	329	510

The specific gravity of distillate and residue are practically equal, while the differences in molecular weight, viscosity index and so forth are remarkably high.

Tables 1 and 2 show the yields obtained, as well as the properties of the products, during gradual increase in pressure.

The asphalts are thrown out of solution at 8 atm. the pressure employed for the propane hydrocarbon. After introducing methane at 40 atm. coloring matter of aromatic nature is precipitated. In spite of a very high viscosity at room temperature their molecular weights amount to only 450 — 500.

TABLE 4

Fractionation of Boryslaw residue (Deparaffinized)*

Solvent Used: Propane 45.7 percent, iso-butane 36.5 percent, *n*-butane 14.7 percent.

Pressure (Atm.)	Yield Percent	Specific Gravity 15.6 °C.	Visc. Eng.		V.I.	Visc. Gravity Const.	Pour	Flash Point
			50 °C.	98.8 °C.				
8 (feed)	....	0.948	47.0	4.36	55	0.876	....	256 °C.
60	25.5	0.9925	....	10.35	..	0.923	....	....
80	34.6	0.958	55.5	4.76	60	0.874	—15	....
100	20.4	0.920	24.7	3.28	82	0.845	—12	....
Residue	15.4	0.895	9.66	2.12	92	0.825	—10	....

*Przemysl Chem. L. C.

Heavier oil fractions separate as a second phase on further increase in pressure. Consequently there are three principal fractions precipitated in the new process:

Asphaltic matter. Color constituents, and lubricating-oils.[7]

The lubricating oils may be further fractionated as shown in the tables. Their properties may be further improved by repeated cold fractionation or by the use of solvent cresol.[8] If cresol is added to a solution of heavy hydrocarbons in propane, then after introducing natural gas by pressure, a solution of hydrocarbons in cresol is precipitated as a second liquid phase of the originally homogeneous mixture. Upon further addition of natural gas, the cresol solution is gradually separated into two phases again; we have therefore an equilibrium state of three phases, which are liquid. The lowest phase consists of cresol saturated with aromatics, with a small quantity of light hydrocarbons; the middle phase consists chiefly of heavy hydrocarbons, and the uppermost portion contains the propane-methane solution with small quantities of oil and cresol.

The bad effects of high temperatures on high molecular weight oils can hardly be entirely avoided by distillation under high vacuum. Many similar investigations have been carried out by other researchers in this field. The Union Oil Company of California[9] claims to extract asphalt-base oils successively with liquefied hydrocarbons that are gaseous at ordinary temperatures. The oil is at first extracted with pentane, then with butane propane, and finally with ethane gas. Besides the precipitated asphalt, lube oils of very low Conradson carbon value are recovered. Ethylene, propylene, butylene, etc., may also be used in the same process.

The Standard Oil Development Company,[10] treats deasphaltized oils with three to five-fold the amount of liquefied (ordinary gaseous) hydrocarbons, having one to five carbon atoms, in order to fractionate the oils to be treated into naphthenic and paraffinic hydrocarbons; the mixtures they employ are said to consist of 15-85 percent ethane and 85-15 percent propane. By altering the treating temperatures or the percentage composition of the slovent mixtures, final lube-oil products of various properties may be obtained.

This process is very similar to that of Pilat, whereas the treating with methane seems to be more efficacious than the successive extraction of Bray. In tables 3 and 4 it is shown how residues from Roumanian, Venezuelan, Polish and Colombian crudes may be treated by cold fractionation without difficulty.

The dark-colored products precipitated by methane at low pressures (30-50 atm.) are supposed to be identical with those precipitated by sulphuric acid during sulphonation in acid-treating. The properties of these products may be seen from Tables 3 and 4. A feature of interest of the above method is that for the first time a number of different oil fractions have been prepared at room temperatures without the use of heat or chemicals. Furthermore, these cold-fractionated lubricants possess better colors and transparency, with much better viscosity indices than do oils made from the same crudes by distillation and acid treatment.[11]

[1] Polish Pat. 1029; German Pat. 362458.
[2] S. v. Pilat: Oel u. Kohle, Erdol u. Teer, 11,655 (1935) Pol. Pat. 20607, of 6.2.33; Prezeml, Chem. 18, 376, 1934.
[3] Brennstoff-Chemie, 4, 17, (1923).
[4] Jour. Ind. Eng. Chem., 23, 548, (1931).
[5] Jour. Ind. Eng. Chem. 26, 214, (1934).
[6] Oil and Gas Jour. 25, 4, 1935, page 13.
[7] The separated oil fractions still contain propane and methane at the pressure of the reaction vessel; these gases may be removed by gentle warming.
[8] Przemysl Chem., 18, 376, (1934).
[9] Ulric Bray U. S. Pat. 1, 988,713, (1932); Chem. Zentralbl, II, 314, 1935.
[10] French Pat. 770,903, 1934; U. S. prior June 10, 1933.
[11] Przemysl, Chem, l.c.

Experimental and Process Development (*Continued from page 109*)

Here each stage of the process is figured by itself, and to begin each new operation 100 gallons of the finished product of the preceding stage is taken and is charged in at the cost per gallon found for that stage. All costs for processing the 100 gallons are set down, credits are given for any side products and the total net cost is divided by the yield to give the cost per gallon on that part of the process. The side products produced will in all probability be of types for which refinery costs already exist, and they can be credited to the operation at these values. All such values should be secured from the cost and yields department. This applies both to the values of oil stocks and to the costs of established operations. This procedure is followed from stage to stage until the oil is finally finished.

Such a method gives the figures life. You show how the wheels go around and what it costs to keep them going. This is particularly necessary when you are presenting a new proposition which you may understand fully but which is not known to the men who finally pass on the reports except as you show it to them. Not only is it new to them but more likely than not they are not any too keen for a change. They have neither the time nor the inclination to dig their way through a complicated mass of figures or to separate and visualize each stage for themselves. If you want consideration for things as you see them you must paint your picture clearly, and not make it necessary for others to paint it for you.

In the regular line of petroleum process development and experimental work the element of judgment plays a greater part than it does in the same class of work in the chemical industry. We do many things for no other reason than the fact that they give us the results we want. We can put no higher mathematics on them nor can we put our fingers on the exact compounds with which we deal. It is possible, however, to systematize procedures, to keep them accurate, to account for everything and then by regular plant accounting methods tie the whole together and lay it out so that it will be clear to any qualified oil man. To lay a basis for such work has been the purpose of this discussion.

Design of Laboratories (*Continued from page 115*)

whole laboratory should be located either centrally or in what might be called the frequency center by which is meant closest to those who use it most frequently. A system of progression for samples should be worked out. Ample facilities as to gas, steam, compressed air, electric outlets, and water should be provided. Each section of desk should be provided with one or more outlets for each of these facilities. Each section of desk should be provided with sink and waste jar facilities; the practice of putting sinks and waste jars only at the ends of work desks is extremely pernicious as it causes crowding and necessitates that the chemist leave his work every time he needs to wash a piece of equipment, draw a bit of water, or throw away some waste. In general necessary bits of apparatus such as hot boxes, hot plates, and hoods should be in small, scattered and easily accessible units rather than in large single units. When small units are used for specific tests, these units should be designed especially for these tests. For instance a hot plate for use in the determination of sediments and insolubles by the reflux method should be long enough for about six to eight extraction flasks and of the width of one extraction flask, and be provided with an edging to keep the flasks on the plate as well as with a suitable rack to hold the reflux columns. Small hood units in the shape of a large funnel attached to the vacuum line which may be turned on or off at the operator's need should be provided every man who handles fuming materials. Suitable glassware racks will materially reduce the breakage bill. Chemical and equipment storage should be as centrally located as is compatible with the factors of safety and worker convenience.

Provision for future expansion is a highly complex question containing as it does a large element of uncertainty and the probability of new testing methods and equipment. For instance it is not improbable that while the testing of light oils seems more or less standardized, the testing of lubricating materials may undergo a very radical change in the near future necessitating the installation of new equipment. This is a problem on which only a careful study of individual problems can throw any light. In conclusion anyone considering the rebuilding of an old or the construction of a new laboratory should not only consult an expert architect or engineer but those graduates of a hard school, the laboratory workers themselves.

Nomographic Charts

for Determining the Fluid Friction in

Pipe Lines

H. V. BECK

Assistant Professor, School of Mechanical Engineering, The University of Oklahoma

THE friction factors shown on these charts are from the authoritative data assembled by Stanton and Pannell and published in the Collected Researches of the National Physical Laboratory, London. Their research was with smooth walled brass pipe and consequently yielded lower friction factors than those found by other investigators whose apparatus consisted of commercial pipe of small diameter. Obviously, the frictional resistance would be greater within the rougher walls of small diameter commercial pipe. This surface roughness of the pipe is, however, a relative thing and is of decreasing importance as the diameter becomes larger. For pipes of the diameters commonly used for the transportation of crude oils, the friction factors are practically identical with the factors for smooth walled pipe.

In order to explain the use of the charts, the following illustrative problem will be considered. Determine the pressure drop per mile in a 10-inch line caused by a flow of 1150 barrels per hour. The fluid has a gravity of 38 degrees A.P.I. and a viscosity of 62 Saybolt seconds.

In order to determine the friction factor it will be necessary to ascertain the Reynolds Number corresponding to the flow conditions. This value is obtained from the first chart in the following manner. A straight line is drawn from the flow in barrels per hour, 1150, to the pipe diameter in inches, 10, intersecting the intermediate dummy scale. From this point of intersection, a straight line is drawn to either of the coincident viscosity scales, 62 Saybolt seconds or its equivalent, a kinematic viscosity of 0.000116.

TABLE 1
Pipe Diameter Table

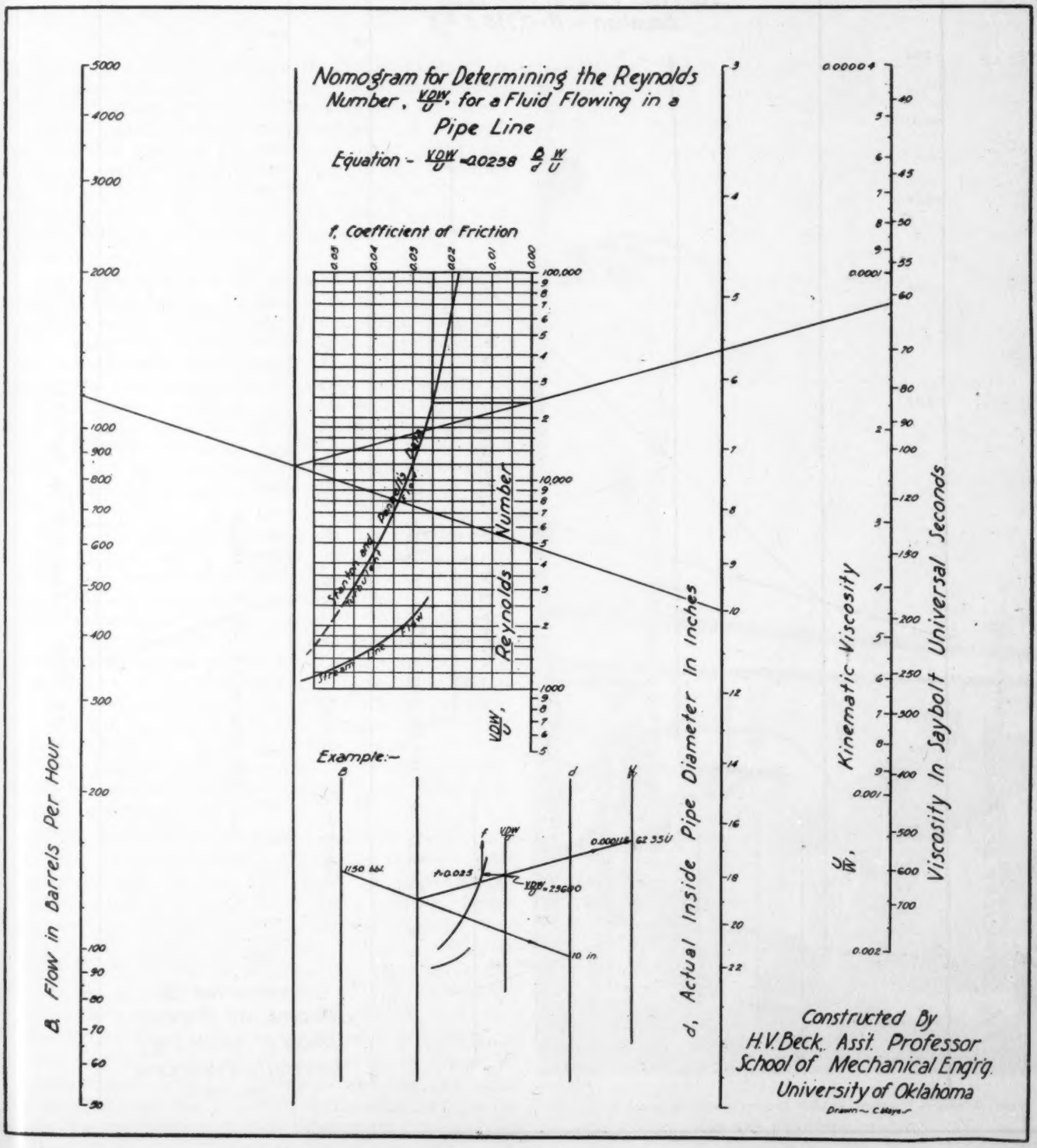
Nominal Diameter, Inches	Actual Diameter, Inches
4	4.026
6	6.065
8	7.982
10	10.02
12	12.00
14	13.25
16	15.25

THESE charts, described in this article, are for the determination of the frictional resistance to a fluid flowing in a pipe line. They are of the same type as those published in a recent issue and have the same distinct advantages listed in that article. In the article referred to, "Nomographic Charts for Measuring Flow of Viscous Fluids," it was explained that the coefficient of a differential producing meter was a function of the Reynolds Number corresponding to the conditions of flow. This criterion—the product of the diameter in feet, the velocity in feet per second, and the reciprocal of the kinematic viscosity—has been found to be the ideal coordinate for graphing the friction factor of a pipe line. When plotted against this coordinate, a single curve represents the variation of the friction factor for any fluid, liquid or gas.

The intersection of this line with the Reynolds Number scale indicates the criterion of flow. The Reynolds Number scale is used as a coordinate of the friction factor graph. For the illustrative example, the Reynolds Number is 23,600 with a corresponding friction factor of 0.025.

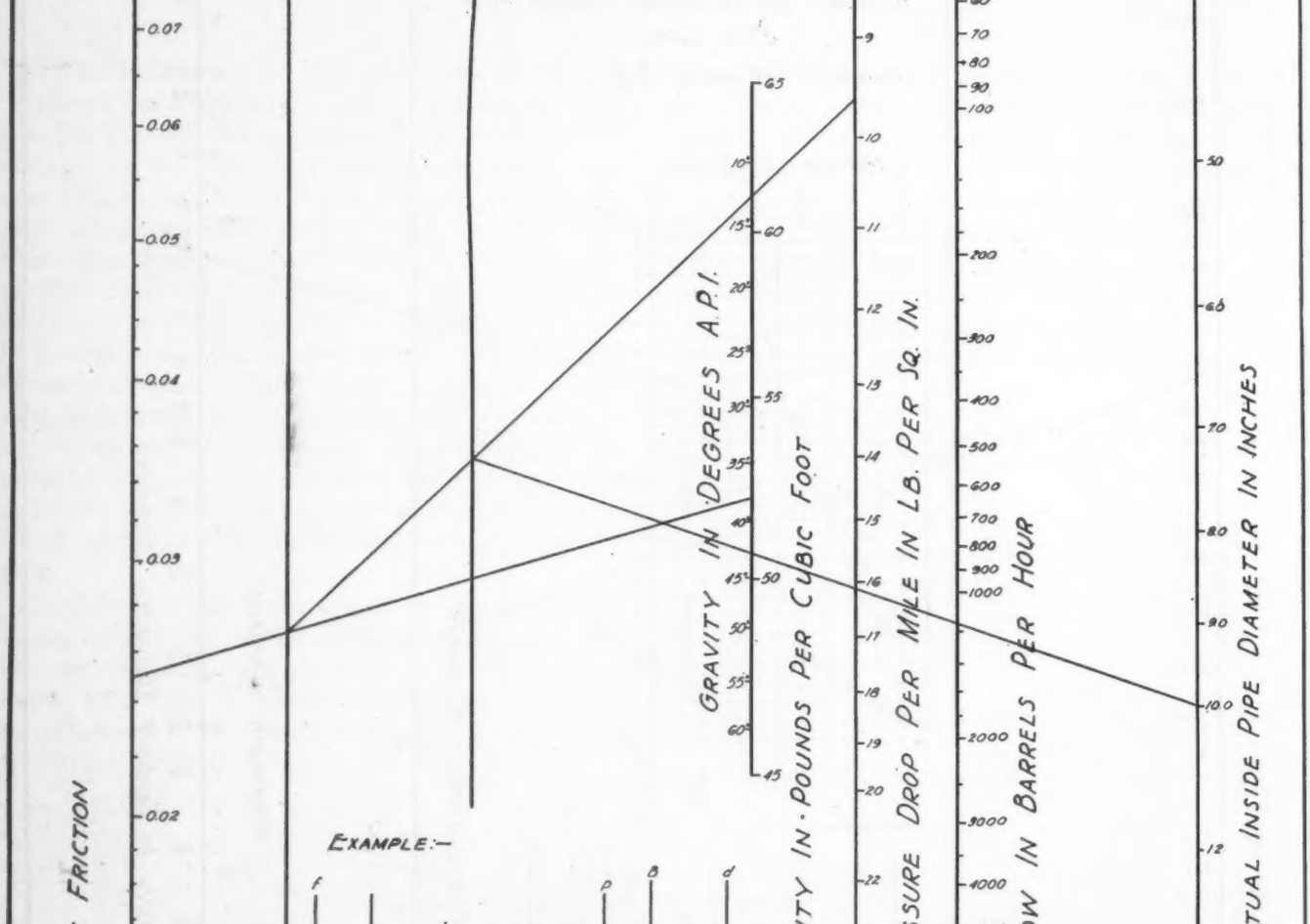
After the friction factor has been determined the computation can proceed on the second chart. A straight line is drawn from the friction factor, 0.025, to the gravity, 38 degrees A.P.I., intersecting the left dummy scale. A straight line is next drawn from the pipe diameter in inches, 10, through the flow in barrels per hour, 1150, and continuing to a point of intersection with the right dummy scale. A straight line is next drawn through the points of intersection on the two dummy scales and continuing on to a point of intersection with the pressure drop scale. This point indicates the solution, a required pressure drop of 9.62 pounds per square inch per mile.

It can be seen that the pressure drop varies inversely as the fifth power of the diameter. Because of this it is quite necessary that the actual inside



pipe diameters be used. To illustrate this variation and to facilitate use of the chart a few of the most common values are listed in Table 1.

In the above illustrative example the manipulations necessary for the solution have been made in a definite order. It is obvious, however, that the calculations may be made in any order, the order depending upon which of the factors are known. It is often necessary that a "cut and try" method be employed; but this method, under those conditions, would be necessary regardless of whether charts or the basic equations were used.



Design of

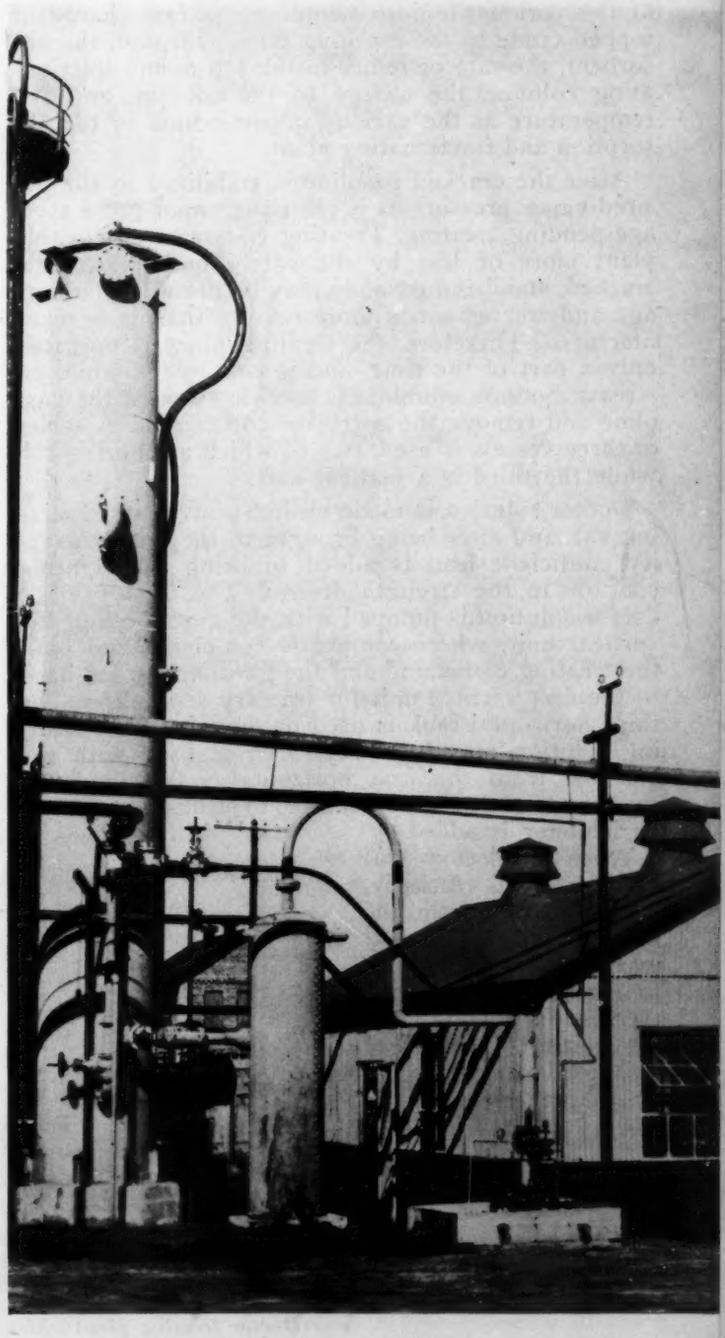
Vapor Recovery Plant *and* Treating Unit *At* CUSHING

SIMULTANEOUSLY with the building of a cracking unit, Cushing Gasoline & Refining Company at Cushing, Oklahoma, installed a vapor-recovery unit together with a sweetening plant to treat the cracked gasoline.The vapor-recovery plant operates in conjunction with the cracking unit by using the topped crude charged to the cracking unit as an absorption oil in the column. The topped crude used for this purpose is the usual product of the skimming units.

The crude is picked up by a reciprocating pump used for charging the topped crude through the exchangers to the fractionating column. The light gasoline vapors are flashed out with the other products and combine with the cracked vapors to be condensed in the regular manner. No distillation unit is used to strip the topped crude of its vapors picked up in the absorber other than the regular cracking equipment. Gases made by cracking topped crude are stripped clean of all desirable constituents in this way, and the expense of operating the absorption unit is thus lowered.

Automatic controls are used on the cold topped-crude charge, which regulate the charging pump speed, and permit a constant flow of crude to the unit. The cracking operation is carried out at the same pressure and temperature at all times, therefore the relation of vapors to charged crude remains approximately the same. Because of this condition, the rate of flow of the charged crude is not determined by the amount of vapors removed from the accumulator drum, as it would be if a regular refinery cut of absorption oil was used in the column. (In The Refiner, August, 1935, Page 396, the cracking operations as practiced at the Cushing plant were presented in detail.)

About 900 barrels of cracked gasoline and recovered vapors are produced daily by the Dubbs cracking plant and the recovery unit, all of which is stabilized before treating with doctor solution. Process pressure is used to force the vapors from the accumulator drum through the absorber column, which is operated at 38 pounds. Two lines leave the top of the accumulator drum, one of which normally carries the vapors and uncondensed gasoline, and the other is connected to a safety pop valve and leads to a vent line where the vapors will escape to the air if excessive pressures are generated and the gas fails to pass through the absorber. All unabsorbed gases from the top of the absorber column are collected in



Vapor recovery plant where topped crude is used as the absorbing medium.

the regular plant fuel lines, and burned under the boilers at the cracking still.

The cracked gasoline, plus the recovered vapors, are fed to a Petroleum Engineering Inc. type of stabilizing column where it is processed at 160 pounds pressure. The reboiler is carried at 332° F. in order that a product having a vapor pressure of eight pounds, Reid, can be manufactured. Overhead uncondensible gases, or those not desired in the finished cracked gasoline, are turned into the plant fuel lines and consumed as fuel. Constant level is maintained in the reboiler and the fractionator through the use of a liquid level controller mounted near the reboiler unit and operating by remote control an outlet valve which permits the finished stabilized cracked gasoline to flow to the proper storage vessels.

Control instruments are located on a board inside the pump room which takes care of the rate of flow of the various liquids, including the raw charge of topped crude to the cracking plant (through the absorber), the rate of reflux to the top of the fractionating column, the charge to the column, and the temperature at the various salient points in the absorption and fractionating plant.

After the cracked gasoline is stabilized to the desired vapor pressure, it is placed in vapor-proof storage pending treating. Treating is carried out in this plant more or less by the batch method, for the cracked, stabilized gasoline may be drawn from storage and treated much more rapidly than it is manufactured. Therefore, the treating plant is operated only a part of the time, and is continuous while on stream. Sodium plumbite is used to sweeten the gasoline and remove the corrosive compounds. A series of three vessels is used, two of which are horizontal, while the third is a vertical unit.

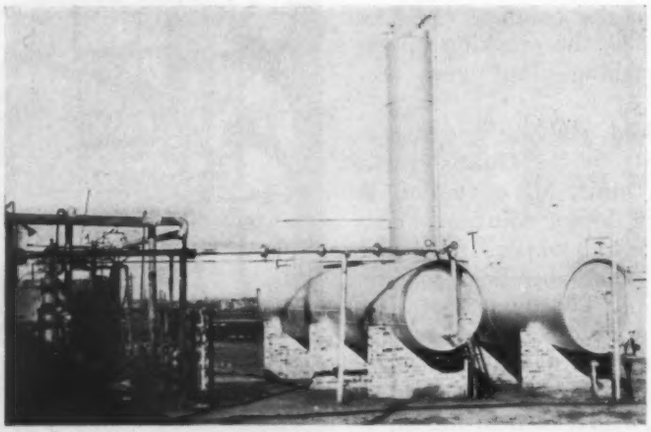
Doctor solution is made up in a conventional mixing vat, and after being brought to the proper gravity, sufficient lead is added to bring the treating solution to the strength desired. The freshly made doctor solution is pumped with the gasoline into the vertical unit, where contact is completed and both the treating compound and the gasoline are led back to the first vertical unit for primary separation. The third horizontal tank is used to separate what treating solution may have been carried over with the gasoline from the first horizontal vessel, and the gasoline, after settling, is removed to plant storage where an inhibitor is added.

When the doctor solution has lost its efficiency, it is removed from the system and placed in a vat where it is blown with air to regenerate it for further use in treating. This vat is an old condenser tank, used many years ago by a predecessor while skimming Cushing crude but still remains on the original elevated supports. Perforated piping was placed in the bottom of this vat and air, pumped by a steam-driven air compressor, is forced through the liquid until most of the undesirable sulfur compounds have been oxidized and removed to the atmosphere. One advantage obtained by using this condenser vat is that the height of the vessel makes it necessary only to pump or blow the spent doctor to the elevation, and after sufficient blowing, it is removed by gravity to the finishing tanks near the original mixing vessels. Here it is heated by submerged coils and blown to finish it for further use. Steam coils are used in these finishing vats to provide the necessary temperature to remove the remaining undesirable sulfur compounds, and the batch, with the addition of a small amount of steamed caustic, and the addition of more lead, is ready to be used again.

All gasoline storage tanks are vapor tight and the vapors are used again in the absorption unit, pressure sufficient to drive them through the column being held on the treating unit so they will travel through and contact with the topped crude where they are recovered and salvaged. The operation of this treating unit is efficient and economical. The gasoline leaving the treating unit has a color value of 30+ and is sweet and non-corrosive. The cost, including the addition of the inhibitor, is on an average of about five cents per barrel of treated liquids.

The operation of the two plants is simplified by the use of control instruments which govern the flow of crude in the first contact, the flow of gasoline to the stabilizer, and the amount of reflux pumped to the top of the column. Close clearance pumps are used to handle the liquids, including the topped crude, so that a precise amount can be handled without racing, or slowing down the pumps. The air compressor is operated at a constant speed, and the volume of air used in regenerating the spent doctor solution is sufficient to obtain the desired results. All of the pumps and control instruments used in the absorption and fractionating processes are housed in one building, where an operator checks the results. The treating pumps are located near the mixing vats and a man is detailed to the operation of the treating plant. The sulfur pot is situated near the gasoline pump, and a split stream of gasoline is used to dissolve the required amount of stick sulfur to complete the reaction while contacting with doctor solution.

Lubricated cast iron plug valves are used almost exclusively on the caustic and gasoline circuits in the treating plant to prevent loss of liquids due to corrosion of metallic surfaces.



Doctor treating plant which handles stabilized pressure distillate and recovery gasoline. Cushing Gasoline & Refining Company, Cushing, Oklahoma.